ISSN 2744-2640

e-ISSN 2744-2659

JST&M, Vol. 2

www.mtf.unze.ba

03

Journal of **Sustainable Technologies and Materials**

Zenica, December 2022

Journal of Sustainable Technologies and Materials (ISSN 2744-2640)
Vol. 2, No. 3(2022), 1 – 39

Published by
The University of Zenica, Faculty of Metallurgy and Technology

Editorial office
Travnička cesta 1,72000 Zenica
Bosnia and Herzegovina
Phone: +387 32 403 468
Email: jstm@unze.ba
Website: https://www.mtf.unze.ba

Editor-in-Chief
Farzet Bikić, The University of Zenica, Faculty of Metallurgy and Technology, B&H

Associate Editors
Hasan Avdušinović, B&H, University of Zenica, Faculty of Metallurgy and Technology
Ilhan Bušatlić, B&H, University of Zenica, Faculty of Metallurgy and Technology
Diana Ćubela, B&H, University of Zenica, Faculty of Metallurgy and Technology
Jusuf Duraković, B&H, University of Zenica, Faculty of Metallurgy and Technology
Almaida Gigović-Gekić, B&H, University of Zenica, Faculty of Metallurgy and Technology
Adnan Mujkanović, B&H, University of Zenica, Faculty of Metallurgy and Technology

Editorial Board Members
Elvis Ahmetović, B&H, University of Tuzla, Faculty of Technology,
Ljubiša Balanović, Serbia, University of Belgrade, Technical Faculty Bor,
Mirjana Čurlin, Croatia, University of Zagreb, Faculty of Food Technology and Biotechnology
Sead Ćatić, B&H, University of Tuzla, Faculty of Technology
Kemal Delijić, Montenegro, University of Montenegro, Faculty of Metallurgy and Technology,
Natalija Dolić, Croatia, University of Zagreb, Faculty of Metallurgy Sisak,
Mirko Gojić, Croatia, University of Zagreb, Faculty of Metallurgy Sisak
Nenad Gubeljak, Slovenia,
The University of Maribor, Faculty of Mechanical Engineering,
Safija Herenda, B&H, University of Sarajevo, Faculty of Science
Nusret Imamović, B&H, University of Zenica, Faculty of Mechanical Engineering
Fehim Korać, B&H, University of Sarajevo, Faculty of Sciences
Borut Kosec, Slovenia, University of Ljubljana, Faculty of Natural Sciences and Engineering
Tibela Landeka Dragičević, Croatia, University of Zagreb, Faculty of Food Technology and Biotechnology
Dragan Manasijević, Serbia, University of Belgrade, Technical Faculty Bor
Sanja Martinović, Serbia, University of Belgrade, Faculty of Technology and Metallurgy
Viorica Musat, Romania, "Dunărea de Jos" University of Galati, **Aleš Nagode**, Slovenia, University of Ljubljana, Faculty of Natural Sciences and Engineering.
Vesna Ocelić Bulatović, Croatia, University of Zagreb, Faculty of Metallurgy Sisak
Iulian Riposan, Romania, University Politehnica of Bucharest, Materials Science and Engineering Faculty
Luca Sportelli, New Zealand, St. Clements University, Niue,
Aida Šapčanin, B&H, University of Sarajevo, Faculty of Pharmacy
Nada Štrbac, Serbia, University of Belgrade, Technical Faculty Bor
Anita Štrkalj, Croatia, University of Zagreb, Faculty of Metallurgy Sisak,
Iveta Vaskova, Slovakia, Technical University of Košice, Faculty of Materials, Metallurgy and Recycling,
Asim Vehbi, North Cyprus,
Arkin University of Creative Arts and Design (ARUCAD)
Milica Vlahović, Serbia, University of Belgrade, Faculty of Technology and Metallurgy,
Tatjana Volkov-Husović, Serbia, University of Belgrade, Faculty of Technology and Metallurgy,
Zdenka Zovko Brodarac, Croatia, University of Zagreb, Faculty of Metallurgy Sisak,

English Language Editor
Hasan Avdušinović, University of Zenica, Faculty of Metallurgy and Technology, B&H
Diana Ćubela, University of Zenica, Faculty of Metallurgy and Technology, B&H

For submission instructions, manuscript submission, and additional information, please visit https://www.mtf.unze.ba/.

Disclaimer: The Publisher and Editors cannot be held responsible for errors or any consequences arising from the use of the information contained in this journal. The views and opinions expressed do not necessarily reflect those of the Publisher and Editors, and neither does the publication of advertisements constitute any endorsement by the Publisher and Editors of the product advertised.

Computer design
Safet Hamedović, University of Zenica, Faculty of Metallurgy and Technology

Cover design:
Admir Velić

Printed by „Štamparija Fojnica" D.D.
Fojnica, B&H, in December 2022

Journal of Sustainable Technologies and Materials JSTM

CONTENTS

1. ***Comparison of Electrocoagulation Coupled with Synthetic Zeolite, Ultrasound and Two Steps Electrocoagulation*** ***1***
   Nediljka Vukojević Medvidović, Ladislav Vrsalović, Sandra Svilović, Mirjana Cestarić

2. ***Leucobryum Glauculum Moss as a Biosorbent for Removal of Water Hardness*** ***11***
   Armin Buljubašić, Vedran Stuhli, Abdel Đozić, Mirnesa Zohorović, Amra Odobašić

3. ***Intensification of Low-Carbon Steel Desulphurisation in the Induction Furnace*** ***17***
   Raza Sunulahpašić, Aida Imamović, Hasan Avdušinović

4. ***Influence of Boron, Zirconium, and Tellurium on the Impact Toughness of X8CrNiS18-9 Steel*** ***24***
   Derviš Mujagić, Aida Imamović, Mustafa Hadžalić

5. ***The Influence of Process Parameters on Brown Stock Pulp Washing at Natron-Hayat Maglaj*** ***31***
   Armina Čamić, Šefkija Botonjić

JST&M 3(2022), 1 - 10
DOI: 10.57131/jstm.2022.3.1

Original scientific paper

COMPARISON OF ELECTROCOAGULATION COUPLED WITH SYNTHETIC ZEOLITE, ULTRASOUND AND TWO STEPS ELECTROCOAGULATION

Nediljka Vukojević Medvidović, Ladislav Vrsalović, Sandra Svilović and Mirjana Cestarić

University of Split, Faculty of Chemistry and Technology

ABSTRACT

Due to the very complex composition of leachate wastewater, combining two or more physical, chemical, or biological processes, carried out simultaneously or sequentially, is highly needed in order to obtain effluent suitable for further discharge into sewage. In this paper, electrocoagulation coupled with synthetic zeolite (EC-NaX), electrocoagulation coupled with ultrasound (EC-US), and two steps electrocoagulation (EC-1st and EC-2nd) were tested for compost leachate treatment, with very high initial organic loading and acidic pH. The comparison of each process was done in regard to the following parameters: pH, electrical conductivity and temperature change, removal percentage of chemical oxygen demand (COD), turbidity, total solids change, settling ability, and electrode consumption. Results highlight the EC-NaX as the best option for the treatment of compost leachate, due to the highest removal percentage of COD (51.91%), satisfactory removal percentage of turbidity (97%), good settling abilities, and lowest electrode consumption. However, the final COD values in the effluent are still significantly high for further discharge into sewage systems, thus additional treatment needs to be applied. Also, the final acidic pH, high values of electrical conductivity, and high temperature of effluent need to be solved in further treatment steps.

Keywords: Al-electrode, coupled electrocoagulation, synthetic zeolite, ultrasound, two-step

Corresponding Author:
Nediljka Vukojević Medvidović
Faculty of Chemistry and Technology in Split
Ruđer Bošković 35, 21000 Split, Croatia
Tel.: + 385 21 329 452; fax: + 385 21 329 461
E-mail address: nvukojev@ktf-split.hr

1. INTRODUCTION

Rapid industrial and technological development during the 20th century brought a huge number of innovations and benefits for humanity, but at the same time increased the negative impact on the environment, which has recently become a global problem. With the entry into the 21st century, technological investigation connected with the reduction of the emission of harmful substances into the environment is intensified. These investigations are also conducted with the purpose to harmonize the preservation and protection of the environment with further industrial development. Wastewater treatment has become one of the biggest challenges for today's engineers as the legislative regulations are becoming stricter and require very low concentrations of harmful substances in wastewater discharged into the environment. Therefore, there is an increased interest in the development of technological solutions that will provide us with the most effective, fastest, most economical, and environmentally friendly way to treat wastewater [1,2]. Electrocoagulation is well known as a promising polishing step in wastewater treatment [3]. Due to its simplicity, accessibility, efficiency, shortness considering the consumed time, and low production of sludge, the electrocoagulation process is potentially one of the most cost-effective wastewater treatment procedures [4,5]. Electrocoagulation is carried out in an electrochemical reactor (cell) equipped with electrodes (at least one anode and cathode), and by introducing direct current into the aqueous medium. The electrocoagulation process consists of destabilizing suspension, emulsion, or dissolved contaminants using three different mechanisms: electrochemical reactions, coagulation, and flotation [6,7]. In the process of electrocoagulation, aluminum and iron electrodes are most often used due to their relatively low price, easy availability, and high efficiency in removing harmful substances. Various studies have shown higher efficiency of aluminum electrodes in the removal of dissolved harmful organic substances compared to other electrodes [8].

However, due to the increased complexity of the composition of produced wastewater, the application of EC as a stand-alone is not enough to obtain effluent suitable for further discharge into sewage. Recently, efforts are being made to develop hybrid or combined processes, which combine EC with other physical, chemical, or biological processes, carried out simultaneously or sequentially (one after the other), in order to overcome the limitations of individual processes [9,10]. An example of such a process is electrocoagulation in combination with zeolite [11,12]. Zeolites are alumosilicates, which can be found in nature or synthesized in laboratory conditions, by simulating hydrothermal processes using elevated temperature or pressure and using natural raw materials and/or synthetic silicates. Zeolite poses good adsorption, ion exchange, and catalytic properties, or can be used as molecular sieves [13]. Combined electrocoagulation with zeolite (performed simultaneously and sequentially) has been investigated recently for the treatment of landfill leachate [14-16], gold mine effluents [12], municipal wastewater [17], and middle-loaded compost leachate [18,19]. Results confirm enhanced removal of COD, ammonium, turbidity, and better settling ability by using combined EC with zeolite addition.

Another example of a combined EC process is electrocoagulation and ultrasound, which combine coagulation, flocculation, and flotation with ultrasonic cavitation. According to Hassani et al. [20], synergistic effects are obtained by improving the physical and chemical changes in the aqueous solution. Sound waves generate pressure fluctuation that leads to enhanced generation of reactive oxygen species and hydroxyl radicals, which results in enhanced mineralization of organic substances [20-22].

Electrocoagulation performed in two steps (sequentially, one after another) is not found in literature, even this feature can be very efficient for the treatment of highly polluted wastewater. Thus, in this paper, three different combinations of EC processes discussed previously were compared for compost leachate treatment with a very high initial organic load and acidic pH. To the best of our knowledge, no such investigation has been performed or published previously. Electrocoagulation coupled with synthetic zeolite (EC-NaX) and electrocoagulation coupled with ultrasound (EC-US) is performed simultaneously, while two steps of electrocoagulation (EC-1st and EC-2nd) are performed sequentially. A comparison was based on measuring the following parameters: pH values, electrical conductivity, temperature, chemical oxygen demand, turbidity, total solids, settling test, and electrode consumption.

2. EXPERIMENTAL SECTION

2.1. Materials

Compost leachate was collected during the composting of biowaste in the "C-EcoForHome" composter with the use of "Compost Help" anaerobic microorganisms. After the anaerobic composting was completed, in the leachate the pH value, electrical conductivity, chemical oxygen consumption (COD), and turbidity were determined, according to the Standard Water and Wastewater Testing Methods [23]. Compost leachate is characterized by acidic pH=4.03, very high organic load (initial COD equals 10427.6 mg O_2/L), a very high electrical conductivity of 3.54 mS/cm, and turbidity of 397 NTU.

Electrode material: The electrodes (cathode and anode) for the electrocoagulation process are made of aluminum alloy AA 2007 series 2000, in which the main alloying element is copper (Al=92.58%, Cu=3.84%).

Synthetic zeolite: The synthetic zeolite purchased from Sigma-Aldrich belonged to the NaX zeolite type with $r_{\mathrm{Si/Al}}$ = 1.23. The zeolite was crushed and sieved into granulations of NaX particles of 160-600 µm.

2.2. Performance of coupled electrocoagulation process

Three different coupled electrocoagulation processes were used for compost leachate treatment: electrocoagulation coupled with synthetic zeolite (EC-NaX), electrocoagulation coupled with ultrasound (EC-US), and two steps of electrocoagulation (EC-1st and EC-2nd). EC-NaX and EC-US are performed simultaneously, while two steps of electrocoagulation (EC-1st and EC-2nd) are performed sequentially.

Electrocoagulation coupled with synthetic zeolite (EC-NaX) was carried out in a 350 mL of electrochemical cell, with immersed electrodes and with the addition of 20 g/L NaX zeolite, without adjusting the initial pH of the solution and without the addition of electrolyte. Distance between electrodes was maintained at 3 cm and a mixing speed of 100 rpm. The applied current density values were i = 0.018 A/m^2, and the working time was 30 min.

In two steps of electrocoagulation (EC-1st and EC-2nd), EC-1st was carried out for 30 minutes under the same conditions previously described but without the addition of zeolite. In the EC-2nd, the volume of 230 mL of solution after the EC-1st with adjustment of initial pH at 6.8 by adding 0.1 mol/l NaOH, was treated again by electrocoagulation for 30 minutes under the same conditions as EC-1st. The efficiency of removal was determined after the first stage and after the second stage.

Electrocoagulation coupled with ultrasound (EC-US) was performed by immersing the electrochemical cell into an ultrasonic bath Asonic Pro, with a reservoir capacity of 3.2 L, which was filled with deionized water. During the electrocoagulation process, a 40 kHz ultrasound was performed. The process of electrocoagulation was carried out for 30 minutes under the same conditions previously described but without the addition of zeolite. Experiments labeling and working conditions are summarized in Table 1.

Table 1. Experiments in labeling and working conditions

Experiments labeling	Working conditions Al electrode, t = 30 min, electrode distance = 3 cm, mixing speed =100 rpm
EC-NaX	EC-NaX (160-600 µm), i = 0.018 A/m^2, NaX addition=20 g/L, without pH adjustment
EC-1st	EC -1st step, i = 0.018 A/m^2, without pH adjustment
EC-2nd	EC-2nd step i = 0.018 A/m^2, pH adjusted at 6.8
EC-US	US-40 kHz, i = 0.018 A/m^2, without pH adjustment

During each process, continuous measurements of pH, electrical conductivity, and temperature were performed, while the COD, turbidity, and total solids (TS) were determined at the beginning and at the end of each experiment. All parameters were determined according to Standard Methods of Water and Wastewater Analysis [23]. After the implementation of coupled EC process, the settling test was conducted according to Kynch. Also, the electrode consumption was determined by weighing of both electrodes (anode and cathode) on analytical balance before and after each experiment.

3. RESULT AND DISCUSSION

3.1. Analysis of pH, electrical conductivity, and temperature during coupled EC processes

3.1.1. Analysis of pH

The results of the pH values, monitored during the coupled electrocoagulation processes are shown in Figure 1.

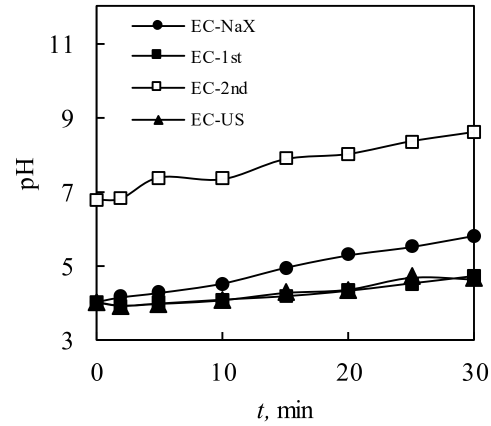


Figure 1. Change of pH value during electrocoagulation coupled with synthetic zeolite (EC-NaX), electrocoagulation coupled with ultrasound (EC-US), and two steps of electrocoagulation (EC-1st and EC-2nd)

The Initial pH value of compost leachate was 4.03. Small continuous increases in pH values were observed during EC-1st and EC-US, while a slightly higher increase is observed in EC-NaX. An increase in pH values during the EC process is expected due to anode dissolution and the water reduction at the cathode, with the formation of hydrogen gas and OH^- ions, which raise the pH of the solution [4,5]. However, the final pH value of the solution reaches only 4.65, 4.71, and 5.83 for EC-1st, EC-US, and EC-NaX processes, respectively. Namely, during the EC process, the pH rise of the solution usually reaches a higher pH value (minimum 8) [17-19]. The reason for obtaining the lower pH value in this study can be attributed to the complex composition of the initial compost leachate solution, which practically acts like a buffer. This was confirmed by adding an additional amount of sodium hydroxide to the initial compost leachate solution before the second step process (EC-2nd), due to which initial pH reached the value of 6.8. The final pH value after EC-2nd was 8.62.

3.1.2. Analysis of electrical conductivity

Changes in the value of electrical conductivity of the solution monitored during the coupled electrocoagulation processes are shown in Figure 2.

For the EC process, the higher conductivity of the solution is an advantage, since the electrical resistance of the solution is, therefore, lower, and it will positively influence on lower electricity consumption [4,5].

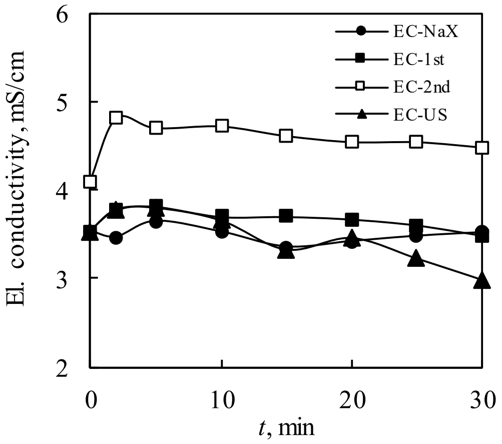


Figure 2. Change in electrical conductivity, expressed in mS/cm, during electrocoagulation coupled with synthetic zeolite (EC-NaX), electrocoagulation coupled with ultrasound (EC-US), and two steps electrocoagulation (EC-1st and EC-2nd)

Observing the experimental data, the initial values of the electrical conductivity of compost leachate equals 3.54 mS/cm. However, the slightly higher initial value of electrical conductivity of the solution is observed at EC-2nd (4.09 mS/cm), due to the addition of the higher amount of OH^- ions and increasing the initial pH values to 6.8. After 2 minutes, a slight increase of electrical conductivity is observed with experiments EC-1st, EC-2nd, and EC-US, followed by a slight decrease. In the experiment with the addition of zeolite (EC-NaX), values of electrical conductivity are oscillating with a slight downward trend. The decreasing trend of electrical conductivity observed at all coupled EC processes can be attributed to the removal of organic particles from the solution.

3.1.3. Analysis of temperature

The results of the temperature change during the implementation of the coupled electrocoagulation processes are shown in Figure 3.

Temperature affects the speed of electrochemical reactions and the formation of flocs, the solubility of metal hydroxides, as well as conductivity of the solution during the electrocoagulation process [5,24]. From the obtained results, a continuous increase in temperature up to cca 33 °C during two steps EC process (EC-1st and EC-2nd) is observed.

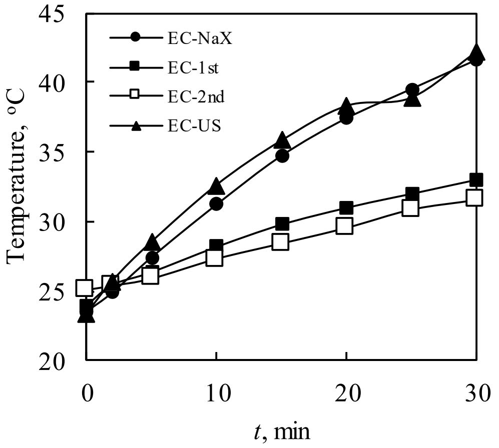


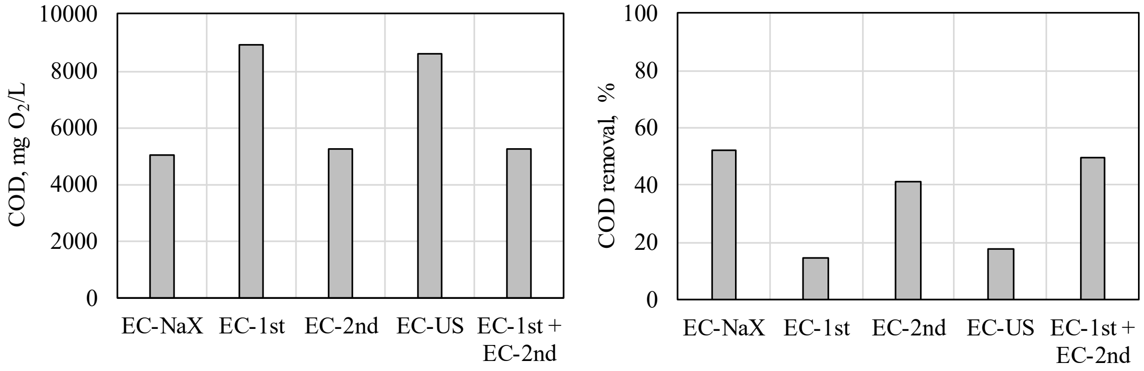
Figure 3. Temperature change during electrocoagulation coupled with synthetic zeolite (EC-NaX), electrocoagulation coupled with ultrasound (EC-US), and two steps of electrocoagulation (EC-1st and EC-2nd)

However, a significantly higher temperature increase is evident with EC-NaX and EC-US, reaching values of 41.6 and 42.2 °C, respectively. For EC-NaX, the temperature increase is probably connected with higher electrode consumption (see Figure 8) and higher removal percentage of COD (51.91%), and turbidity removal (97%). In the case of EC-US, a higher increase in solution temperature can be also the result of the influence of US-bath temperature. Thus, the temperature is a parameter that should be taken into account, as the too high temperature of the final effluent can cause thermal pollution.

3.2. Removal efficiency analysis

3.2.1. Analysis of chemical oxygen demand

Removal efficiency is a critical factor that contributes to the decision-making process on whether to use a combined process or to use the two-step EC process alone. The results of the values of chemical oxygen demand (COD) for each coupled electrocoagulation process are presented in Figure 4.



a) b)

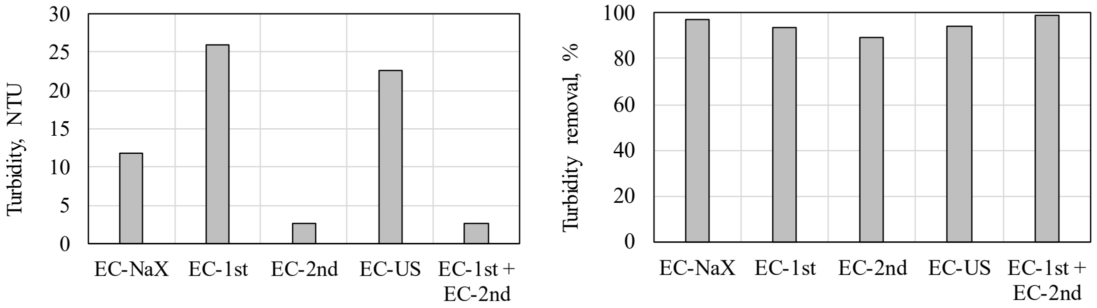
Figure 4. COD values in final solution (a) and COD removal efficiency (b) for electrocoagulation coupled with synthetic zeolite (EC-NaX), electrocoagulation coupled with ultrasound (EC-US), and two steps electrocoagulation (EC-1st and EC-2nd)

The COD value in the initial sample reaches over 10000 mg O_2/L, which indicates a very high total organic loading of compost leachate. From Figure 4, it is evident that the best removal efficiency was obtained with EC-NaX (51.91%), indicating that the addition of zeolite significantly improved the EC process. By carrying out the two-stage process without the addition of zeolite, lower removal percentages were obtained in the 1st stage (only 14.50%). However, the removal percentage in the second stage equals 41.07%, while the total removal percentage of 1st and 2nd gives values of 49.62%, which almost approach the removal percentage of EC-NaX. This indicates a positive effect of conducting the electrocoagulation procedure in two stages. COD removal efficiency obtained by EC-US is not so high (only 17.56%), and it is almost the same order of magnitude as EC-1st stand-alone. According to Asgharian et al [22], the removal of humic acid by EC and US achieves decreasing removal efficiency compared to the EC process alone. This behavior was explained by the fact that the EC process produces clusters of humic acid which can be easily decanted or destroyed while the US waves seem to disrupt the clusters and the coagulated humic acid dissolves again and returns to the solution.

Among coupled EC processes, the following COD removal sequence can be obtained: EC-NaX > EC-1st + EC-2nd > EC-US. However, the final COD values are still significantly high for further discharge into sewage systems, which indicates that coupled EC processes are more applicable for compost leachate with lower total organic loading.

3.2.2. Analysis of turbidity

The results of measuring the turbidity of the composting leachate before and after the application of coupled electrocoagulation processes are shown graphically in Figure 5.



a) b)

Figure 5. Turbidity values in final solution (a) and turbidity removal efficiency (b) for electrocoagulation coupled with synthetic zeolite (EC-NaX), electrocoagulation coupled with ultrasound (EC-US), and two steps electrocoagulation (EC-1st and EC-2nd)

The turbidity value in the initial sample reaches 397 NTU, which indicates general contamination with suspended, colloidal, and dissolved organic matter in compost leachate. Application of all three different treatment systems leads to high percentages of turbidity removal, in the range of 89.54-99.32%. The highest percentage of turbidity removal was recorded using a two-stage electrocoagulation process where the total removal percentage equals 99.32%, an almost clear solution was obtained after the second stage (turbidity in the final solution equals 2.71 NTU). Individually, the removal percentage after EC-1st is 93.48%, while after EC-2nd is 89.54%. A very high removal percentage is obtained with EC-NaX reaching 97%, which indicates a positive effect of combining NaX zeolite and EC compare to single EC-1st. The use of ultrasound (EC-US) also leads to very high percentages of turbidity removal of 94.31%. Among coupled EC processes, the following turbidity removal percentage sequence is obtained: EC-1st + EC-2nd >EC-NaX > EC-US.

3.3. Analysis of the total solids

The results of the total solids (TS) measured in the compost leachate before and after the application of coupled electrocoagulation processes are shown graphically in Figure 6.

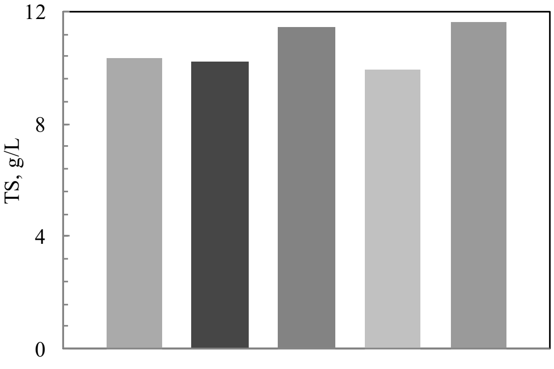


Figure 6. Comparison of TS in initial solution and solution after application of electrocoagulation coupled with synthetic zeolite (EC-NaX), electrocoagulation coupled with ultrasound (EC-US), and two steps electrocoagulation (EC-1st and EC-2nd)

The TS value in the initial sample reaches 10.33 g/L, while its values in solution after the application of coupled electrocoagulation processes are slightly oscillating from the lowest of 9.9 g/L to the highest value of 11.99 g/L. The lowest value of TS in solution was obtained with the EC-NaX and EC-2nd as stand-alone, while slightly higher is obtained with electrocoagulation coupled with ultrasound (EC-1st and EC-US). This can be connected with lower COD removal obtained with EC-1st and EC-US, due to which most of the total solids are retained in the solution.

3.4. Settling test

The results of the settling test in compost leachate after the application of coupled electrocoagulation processes are shown graphically in Figure 7.

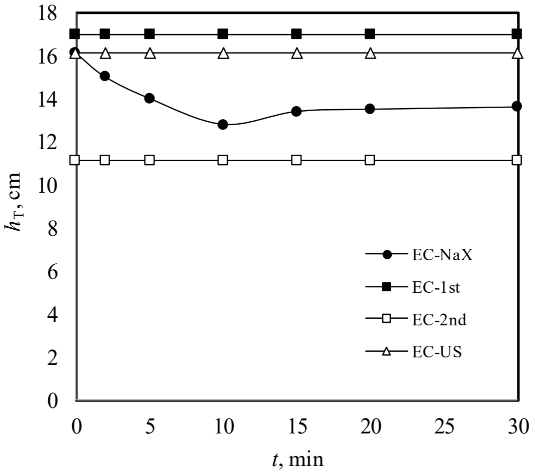


Figure 7. Results of settling test after application of electrocoagulation coupled with synthetic zeolite (EC-NaX), electrocoagulation coupled with ultrasound (EC-US), and two steps of electrocoagulation (EC-1st and EC-2nd)

It can be seen that after the application of electrocoagulation coupled with ultrasound (EC-US) and two steps of electrocoagulation (EC-1st and EC-2nd), there was no settling of particles, ie. the height of the settling column remained unchanged throughout the 30 minutes of the experiment. According to Al-Qodah and Al-Shannag [25], the application of ultrasound energy can cause possible destruction of the formed colloidal hydroxides and the formed adsorption layer on the surface of the colloidal particles which can negatively influence settling abilities. In the case of two steps electrocoagulation (EC-1st and EC-2nd), probably insufficient coagulant dosages of aluminium occur which leads to the formation of products contaminated with other structures, such as residues of non-coagulated pollutants, and residues of 'unused' stable micelles $\{Al(OH)_3\}_n$ or their destabilization products, which have a negative impact on the settling properties [26]. However, after the application of electrocoagulation coupled with synthetic zeolite (EC-NaX), good settling was observed (the height of the column is decreasing compared to the initial value), which confirms that the addition of NaX zeolite significantly improves the settling ability of suspension, which is very important in the practical application of any EC process.

3.5. Electrode consumption analysis

The consumption of electrodes during the experiment was determined by weighing the anode and cathode before and after the electrocoagulation process, and the difference was calculated. The results of the electrode consumption after the application of coupled electrocoagulation processes are shown graphically in Figure 8.

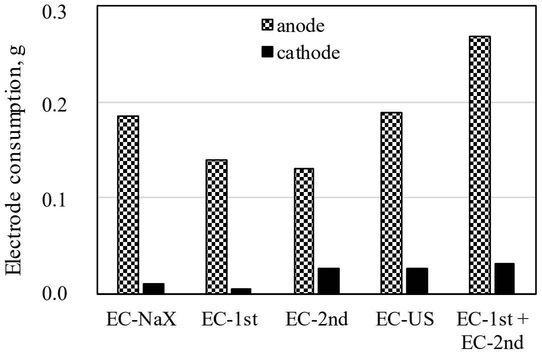


Figure 8. Results of cathode and anode electrode consumption after application electrocoagulation coupled with synthetic zeolite (EC-NaX), electrocoagulation coupled with ultrasound (EC-US), and two steps electrocoagulation (EC-1st and EC-2nd)

In general, the consumption of aluminum electrodes can be explained as a consequence of the electrochemical and chemical dissolution of aluminum. In the case of aluminum electrodes, both anode and cathode consumption occur [27]. From Figure 8, it is evident that the lowest values of electrode consumption are obtained with EC-1st and EC-2nd when they are performed stand-alone, which has a final effect on lower values of increased temperature in solution. Hoverer, if we summarize the electrode consumption, then the highest value of electrodes consumption is obtained with two steps of electrocoagulation (EC-1st and EC-2nd), in which total consumption of anode during both steps reached values of 0.267 g, and total cathode consumption equals 0.033 g. The lowest cathode and anode electrode consumption is obtained by EC-NaX (anode and cathode electrode consumption equals 0.1848 g and 0.011 g, respectively). Slightly higher consumption is obtained with EC-US. Among coupled EC processes, the following sequence for electrode consumption is obtained: EC-1st + EC-2nd > EC-US > EC-NaX.

4. CONCLUSION

Electrocoagulation coupled with synthetic zeolite (EC-NaX) and electrocoagulation coupled with ultrasound (EC-US) performed simultaneously, and two steps electrocoagulation (EC-1st and EC-2nd) performed sequentially, can be successfully applied for compost leachate treatment with very high organic load (initial COD equals 10427.6 mg O_2/L), the very high electrical conductivity of 3.54 mS/cm and turbidity 397 NTU. During the comparison of three different coupled EC processes, the following was observed:

- The complex composition of the compost leachate acts like a buffer, thus only slight increases in pH values (from initial of 4.03 to final 4.65, 4.71, and 5.83 for EC-1st, EC-US, and EC-NaX, respectively) were observed during EC coupled processes. The final pH value of the compost leachate is below the limit values for discharge into surface waters and into the public sewage system (pH=6.5-9.5).
- The decreasing trend of electrical conductivity observed at all coupled processes can be attributed to removal of organic particles from the solution. However, the final values of electrical conductivities are very high (in the range of 2.99-4.48 mS/cm), which can have negative effects in case of discharge into the natural water body.
- Two steps EC process (EC-1st and EC-2nd) are characterized by continuous increases in temperature (up to 33 °C), while a significantly higher temperature increase is evident with EC-NaX and EC-US, reaching values of 41.6 and 42.2 °C, respectively. Having in mind that a higher temperature of final effluent can cause thermal pollution, thus this needs to be solved in practical application.
- The best COD removal efficiency was obtained with EC-NaX, reaching 51.91%. The obtained COD removal sequence is EC-NaX > EC-1st + EC-2nd > EC-US. Even if satisfactory values of removal efficiencies are obtained by the application of all three different coupled EC processes, final COD values are still significantly high for further discharge into sewage systems. This indicates that coupled EC processes should be applied for compost leachate with lower total organic loading, or additional treatment steps need to be applied.
- Percentages of turbidity removal were in the range 89.54-99.32%, with the following turbidity removal percentage sequence: EC-1st + EC-2nd >EC-NaX > EC-US.
- After the application of EC-NaX and EC-2nd as stand-alone, the TS value is slightly lower compared to the initial one of 10.33 g/L, while a slightly higher TS is obtained with EC-US and EC-1st.
- Good settling ability was obtained only with EC-NaX.
- During the EC process using an aluminum electrode, both anode and cathode consumption occur. The following sequence for electrode consumption is obtained: EC-1st + EC-2nd > EC-US > EC-NaX.

Based on obtained results, EC-NaX was found the best option for the treatment of compost leachate with very high organic loading, as the highest values of COD and satisfactory turbidity percentage removal were obtained, good settling ability, and the lowest electrode consumption. Also, treatment time for simultaneous EC-NaX was twice as short compared to two steps electrocoagulation. However, regarding the values of pH in the final solution, high values of electrical conductivity, and high temperature, additional treatment need to be performed in order to obtain effluent suitable for further discharge into sewage.

Future research direction should be focused on analyzing the EC process with other electrode materials which are more environmentally friendly compared to electrodes made from aluminium alloys. Also, proper management of obtained sludge and floating scrum created at the top of suspension during the EC process need to be investigated. Electrode passivation is another focal problem that needs to be solved during EC application. There is some indication that the addition of zeolite and ultrasound may decrease electrode passivation, but future investigations need to be performed in order to prove these findings. In addition to all previously mentioned, recent energy crises require innovation regarding renewable energy sources in order to reduce the high cost of electrical energy consumption during coupled EC processes.

Acknowledgments

The results in this paper are funded by institution funds of the Faculty of Chemical Technology University of Split, Croatia.

Conflict of interest

The authors declare that they have no competing interests.

References

[1] S. A. R. Khan, P. Ponce, Z. Yu, H. Golpîra, M. Mathew, Environmental technology and wastewater treatment: Strategies to achieve environmental sustainability, *Chemosphere,* 286 (2022), p. 131532 https://doi.org/10.1016/j.chemosphere.2021.131532.

[2] P. C. O. Zapata-Mendoza, O. J. Berrios-Tauccaya, V. A. Tirado-Kulieva, J. A. Gonzales-Malca, D. R. Ricse-Reyes, A. A. Berrios-Zevallos, Environmentally Friendly Technologies for Wastewater Treatment in Food Processing Plants: A Bibliometric Analysis, *Sustainability,* 14 (2022) 22, p. 14698 https://doi.org/10.3390/su142214698

[3] Z. Al-Qodah, Y. Al-Qudah, E. Assirey, Combined biological wastewater treatment with electrocoagulation as a post-polishing process: A review, *Sep. Sci. Technol.*, 55 (2020) 13, p. 2334-2352 DOI: 10.1080/01496395.2019.1626891.

[4] I. D. Tegladza, Q. Xu, K. Xu, G. Lv, J. Lu, Electrocoagulation processes: a general review about role of electro-generated floc in pollutant removal, *Process Saf. Environ. Prot.*, 146 (2021), p. 169-189 https://doi.org/10.1016/j.psep.2020.08.048

[5] M. Bharath, B. M. Krishna, B. M. Kumar, A review of electrocoagulation process for wastewater treatment, *Int. J. Chem. Tech. Res.,* 11 (2018), p. 289-302 http://doi.org/10.20902/IJCTR.2018.110333

[6] M. Simonič, M. Čurlin, L. Fras Zemljič, Analysis of electrocoagulation process efficiency of compost leachate with the first order kinetic model, *Holistic Approach Environ.*, 10 (2020), p. 35 – 40, https://hrcak.srce.hr/file/346950

[7] G. Chen, Electrochemical technologies in wastewater treatment, *Sep. Purif. Technol.*, 38 (2004), p. 11-41, DOI:10.1016/j.seppur.2003.10.006

[8] M. Azhar, H. A. Aziz, M. S. Yusoff, S. A. Rezan, Optimization and Analysis of Zeolite Augmented Electrocoagulation Process in the Reduction of High-Strength Ammonia in Saline Landfill Leachate, *Water,* 12 (2020), DOI:10.3390/w12010247

[9] Y. G. Asfaha, A. Kebede Tekile, F. Zewge, Hybrid process of electrocoagulation and electrooxidation system for wastewater treatment: A review, *Cleaner Eng. Technol.,* 4 (2021), p. 100261 https://doi.org/10.1016/j.clet.2021.100261

[10] S. N. A. Jalil, N. Amri, A. A. Ajien, N. F. Ismail, B. A. Ballinger, A hybrid electrocoagulation-adsorption process for fluoride removal from semiconductor wastewater, *J. Phys.: Conf. Ser.,* 1349 (2019), p. 012056, DOI:10.1088/1742-6596/1349/1/012056

[11] A. K. Alenezi, H. A. Hasan, K. S. Hashim, J. Amoako-Attah, M. Gkantou, M. Muradov, P. Kot, B. Abdulhadi, Zeolite-assisted electrocoagulation for remediation of phosphate from calcium-phosphate solution, *IOP Conf. Ser., Mater. Sci. Eng.*, 888 (2020), p. 012031 https://iopscience.iop.org/article/10.1088/1757-899X/888/1/012031/pdf

[12] M. Zolfaghari, S. Magdouli, R. Tanabene, S. P. Komtchou, R. Martial, T. Saffar, Pragmatic strategy for the removal of ammonia from gold mine effluents using a combination of electro-coagulation and zeolite cation exchange processes: A staged approach, *J. Water Proc. Eng.*, 37 (2020), p. 101512

https://doi.org/10.1016/j.jwpe.2020.101512

[13] M. Król, Natural vs. Synthetic Zeolites, *Crystals* 10 (2020), p. 622 https://doi.org/10.3390/cryst10070622

[14] M. A. A. Hamid, H. A. Aziz, M. S. Yusoff, S. Abdul Rezan, Clinoptilolite augmented electrocoagulation process for the reduction of high-strength ammonia and color from stabilized landfill leachate, *Water Environ. Res.*, 93 (2020), p. 1461 https://doi.org/10.1002/wer.1461

[15] M. A. A. Hamid, H. A. Aziz, M. S. Yusoff, S. Abdul Rezan, Optimization and analysis of zeolite augmented electrocoagulation process in the reduction of high-strength ammonia in saline landfill leachate, *Water*, 12 (2020), p. 247 https://doi.org/10.3390/w12010247

[16] M. A. A. Hamid, H. A. Aziz, M. S. Yusoff, S. Abdul Rezan, A continuous clinoptilolite augmented SBR-electrocoagulation process to remove concentrated ammonia and color in landfill leachate, Environ. Technol. Innov. 23 (2021), p. 101575, https://doi.org/10.1016/j.eti.2021.101575

[17] N. Vukojević Medvidović, L. Vrsalović, T. Brozinčević, S. Svilović, *Treatment of municipal wastewater by electrocoagulation and natural zeolite – influence of initial pH values*, In: Book of Abstracts of the 4th International Conference on the Sustainable Energy and Environmental Development, Krakov, Institute of Sustainable Energy, 2021, p. 11

[18] N. Vukojević Medvidović, L. Vrsalović, T. Ugrina, I. Jukić, *Electrocoagulation augmented with natural zeolite—the new hybrid process for treatment of leachate from composting of biowaste*, In: Proceedings of the 19th International Foundrymen Conference: Humans—Valuable Resource for Foundry Industry Development, Split, Croatia, 16–18 June 2021; Faculty of Metallurgy, University of Zagreb, Zagreb, Croatia, 2021, p. 489–498. https://ifc.simet.hr/?page_id=2518

[19] N. Vukojević Medvidović, L. Vrsalović, S. Svilović, A. Bobanović, Electrocoagulation vs. Integrate Electrocoagulation-Natural Zeolite for Treatment of Biowaste Compost Leachate—Whether the Optimum Is Truly Optimal, *Minerals,* 12 (2022), p. 442 https://doi.org/10.3390/min12040442

[20] A. Hassani, M. Malhotra, A. V. Karim, S. Krishnan, P. V. Nidheesh, Recent progress on ultrasound-assisted electrochemical processes: A review on mechanism, reactor strategies, and applications for wastewater treatment, *Environ. Res.*, 205 (2022), p. 112463 https://doi.org/10.1016/j.envres.2021.112463

[21] H. Posavcic, D. Vouk, I. Halkijevic, The effects of ultrasound and electrocoagulation on removal of manganese from wastewater, *Engineering Review,* 42 (2022) 2, p. 1-9 https://doi.org/10.30765/er.1734

[22] F. Asgharian, M. Khosravi-Nikou, B. Anvaripour, and I. Danaee, Electrocoagulation and ultrasonic removal of humic acid from wastewater, *Environ. Prog. Sust. Energy*, 36 (2017) 3, p. 822–829, DOI:10.1002/ep.12512 https://aiche.onlinelibrary.wiley.com/doi/epdf/10.1002/ep.12512

[23] A. D. Eaton, L. S. Clesceri, E. W. Rice, A. E. Greenberg and M. A. H. Franson, *Standard Methods for the Examination of Water & Wastewater*, 21st Edition, American Public Health Association (APHA), American Water Works Association (AWWA) & Water Environment Federation (WEF), Washington, 2005

[24] S. F. Weiss, M. L. Christensen, M. K. Jorgensen, Mechanisms behind pH changes during electrocoagulation, *AIChE J.,* (2021) e17384, https://doi.org/10.1002/aic.17384

[25] Z. Al-Qodah, M. Al-Shannag, On the Performance of Free Radicals Combined Electrocoagulation Treatment Processes, *Separation & Purification Reviews*, 48 (2019), p. 143-158 DOI: 10.1080/15422119.2018.1459700

[26] L. Smoczyńskia, S. Kalinowskia, H. Ratnaweerab, M. Kosobuckaa, M. Trifescua, K. Pieczulis-Smoczyńska, Electrocoagulation of municipal wastewater - a pilot-scale test, *Dealin. Water Treat.*, 72 (2017), p. 162-168 DOI:10.5004/dwt.2017.20645.

[27] D. Ghernaouta, B. Ghernaoutb, A. Boucherita, M. W. Naceura, A. Khelifaa, A. Kelli, Study on mechanism of electrocoagulation with iron electrodes in idealized conditions and electrocoagulation of humic acids solution in batch using aluminium electrodes, *Desalin. Water Treat.,* 8 (2009), p. 91-99 https://doi.org/10.5004/dwt.2009.668

JST&M 3(2022), 11 - 16
DOI: 10.57131/jstm.2022.3.2

JST🌿M

cc BY

Original scientific paper

LEUCOBRYUM GLAUCULUM MOSS AS A BIOSORBENT FOR REMOVAL OF WATER HARDNESS

Armin Buljubašić[1], Vedran Stuhli[2], Abdel Đozić[2], Mirnesa Zohorović[2], Amra Odobašić[3]

[1]University of Tuzla, Faculty of Technology, student of Department of Environmental Engineering
[2]University of Tuzla, Faculty of Technology, Department of Environmental Engineering
[3]University of Tuzla, Faculty of Technology, Department of Physical Chemistry and Electrochemistry

ABSTRACT

Water hardness and deposition of incrustation is a problem in households and industry. In this regard, several technologies have been developed with the purpose of water softening and preventing the deposition of incrustation. The ion exchange method is the most commonly used method and is considered a conventional method. However, due to the shortcomings of this method, there is a need to develop adequate alternative methods. The potential of the method using biosorbents such as moss *Leucobryum glaucum* and *Spaghnum peat moss* for the purpose of removing water hardness has recently become the subject of intensive research with growing interest. In this study, the method using *Leucobryum glaucum* as a biosorbent was tested and a comparison was made with the conventional method and previously conducted studies that used other biosorbents.

Keywords: Ca^{2+}, Mg^{2+}, total hardness, water softening, alternative softening methods, biosorbent

Corresponding Author:
Vedran Stuhli
University of Tuzla, Faculty of Technology, Department of Environmental Engineering
Address, Tuzla, 75000 Tuzla, B&H
Tel./fax: + 387 35 320 793
E-mail address: vedran.stuhli@unitz.ba

1. INTRODUCTION

Water in Bosnia and Herzegovina, with respect to the concentration of dissolved minerals calcium and magnesium, is usually classified as hard water, which results in efforts to soften the water and prevent the harmful effects of scale deposits. Hard water is a big problem both in industry and in households. The most common problems in households are the creation of scale depositions in washing machines and dishwashers and the visible deposition of scale on dishes after washing. Nevertheless, this property of water is a much bigger problem in the industry where the damage is estimated at dozens of billions of dollars a year globally [1]. Scale deposition is a common problem that occurs in heat exchangers in industrial recirculating cooling water systems [2,3]. Scale deposits on the heat exchanger surface are mostly made up of concentrated hardness ions such as Ca^{2+} and Mg^{2+}, which reduce the flow rate and increase energy consumption [4-6].

Taking into account all the mentioned harmful effects of hard water, various methods for its softening have been developed over time. The method currently most widely used and considered the conventional method is the ion exchange method. However, due to the shortcomings of this method, under certain conditions, other methods have predispositions for greater and wider application [7].

In recent considerable attention has been focused on the development and use of low-cost biosorbents based on renewable or waste materials [8-10]. Mosses appear to have great potential in terms of the biosorption of metal ions. However, the exact mechanism of metal ion binding to moss is not well understood. The process of cation sorption, based on the ion exchange between the moss thallus and a solution that wets the thallus, is the most known. The ion-exchange process involves several functional groups, including carboxyl groups (–COOH), aldehyde groups (–CHO), hydroxyl groups (–OH) and amino groups ($-NH_2$), that form part of cell wall-forming compounds, such as lignin-like phenolic compounds [11]. Some authors also point to the possibility of complexing metal ions and physical adsorption [12].

It has been known that *Leucobryum glaucum* from the family of Bryophyta (mosses), has a physical structure that efficiently absorbs metal ions, most notably Zn^{2+} and Cd^{2+} from water [13]. Furthermore, *L. Glaucum* has applications in removing pollutants from wastewater through phytodegradation. Therefore, it is used as an active filtering and adsorption agent for the COD and BOD treatment of wastewater [14].

The aim of this study was to evaluate the ability of the biosorption method using *L. glaucum* to remove Ca^{2+} and Mg^{2+} from water in order to analyze its efficiency in removing water hardness compared to the conventional ion exchange method and previously conducted research using the biosorption method.

2. MATERIALS AND METHODS

2.1. Materials

In all water softening experiments, water from the Tuzla water supply system was used as raw water. For the needs of the experiment of softening water with moss biosorbent, the moss *Leucobryum glaucum* was harvested.

2.2. Methods

2.2.1. Determination of pH value

Electrometric pH measurement was performed by direct measurement of the pH meter METTLER TOLEDO FE 20/EL 20 [15].

2.2.2. Determination of electrical conductivity

Electrometric measurement of the conductivity of the sample was directly measured using a conductometer METTLER TOLEDO FE 20/EL 20.

2.2.3. Determination and calculation of total hardness

The analysis of total hardness was measured using EDTA titrimetric method [16].

2.2.4. Determination of calcium hardness and calculation of calcium content

Determination of calcium hardness was performed using the volumetric titration method with standard solution EDTA. The solution was buffered with 0.1 M NaOH and 0.5 g of Murexid indicator was used. Ca^{2+} concentration was calculated using equation 1:

$$C_{Ca^{2+}} = \frac{560 \cdot V_{EDTA}}{V_S} \tag{1}$$

where is:

- V_{EDTA} - volume used for titration (ml)
- V_S = 100 ml
- $C_{Ca^{2+}}$- mass concentration of Ca^{2+} (mg/l)

Calculation of magnesium content

The concentration of Mg^{2+} has been calculated using equation (2):

$$C_{Mg^{2+}} = \frac{TH - C_{Ca^{2+}}}{7.19} \tag{2}$$

Where is:

$C_{Ca^{2+}}$- Ca^{2+} concentration (°N)
TH – total hardness (°N)
$C_{Mg^{2+}}$- Mg^{2+} concentration (mg/l)

2.2.5. Determination of alkalinity

The analyzed alkalinity parameter was determined by adding four drops of phenophthalein to the sample. If the addition changed the color of the sample to pink, the sample was titrated with 0.1 M hydrochloric acid solution until discoloration. If no discoloration occurs, two drops of methyl orange are added to the same sample. It would then be titrated with 0.1 M hydrochloric acid solution until the color turned orange. The results were expressed in ml of 0.1 M hydrochloric acid required for neutralization per liter of water, and the calculation was performed using equation (3) and equation (4):

$$P\ alkalinity = A_{phph} \cdot 10 \qquad (3)$$
$$M\ alkalinity = A_{mo} \cdot 10 \qquad (4)$$

Where:
A_{phph} - 0.1 M hydrochloric acid solution used for titration with phenophthalein (ml)
A_{mo} - 0.1 M hydrochloric acid solution used for titration with methyl orange (ml)

2.3. Experimental design

2.3.1. Water softening using ion exchange method

The setting of the ion exchange water softening experiment was performed in the form of an improvised ion exchange column consisting of a burette filled with cation ion exchange resin. The raw water was passed through the burette from top to bottom and hence softened water, as a sample to be further analyzed, was continuously collected at the bottom of the burette. 1500 mL of water was treated and used to form 15 samples with a volume of 100 mL. Samples were analyzed in order to obtain relevant parameters using the methodology described in the previous section. Due to its high prevalence, this method is the reference method in this study.

2.3.2. Water softening experiment using *L. glaucum* as a biosorbent

The moss was cleaned and traces of earth and other impurities were removed. The research was conducted in two series of samples. In the first setup, 15 g of cleaned moss was weighed, crushed, and mixed with 1500 mL (0.01 g/mL) of water. The mixture was stirred for 5 minutes after which it was filtered. To prepare the second setup, 30 g of moss was weighed and put in 1500 mL (0.02 g/mL) of water. The rest of the procedure was basically the same as in the previous setups. The obtained filtrate, in both setups, was used to prepare 15 samples per 100 mL volume of sample, which were used to determine the above-mentioned parameters according to the methodology described in the Methods section.

3. RESULTS AND DISCUSSION

Based on laboratory tests of water softening, the results shown in Table 1 were obtained and total hardness, $Ca^{2+,}$ and Mg^{2+} removal percentages for different methods and their mass concentrations were calculated and shown in Table 2.

Table 1. Measured experimental results (EC – electroconductivity, TH – total hardness, $Ca^{2+,}$, and Mg^{2+}- Ca^{2+} and Mg^{2+}concentrations, P and M – P and M alkalinity)

Parameter		pH	EC	TH	Ca^{2+}	Mg^{2+}	P	M
Unit		-	(µS/cm)	(°N)	(mg/L)	(mg/L)	-	-
Tap water		7.2	499.6	14	86.9	38.2	40.7	40.6
Ion exchange method		2.7	507	3.6	18.6	12.9	0	0
Softening method using	0.01 g/mL	6.8	443	10.8	63.8	32.2	33.6	33.6
L. glaucum biosorbent	0.02 g/mL	6.6	284.3	5.7	41.8	11.1	34.6	34.6

Table 2. Total hardness, Ca^{2+} and Mg^{2+} removal percentage obtained in the study

Parameter		TH	Ca^{2+}	Mg^{2+}
Unit		(Removal %)	(Removal %)	(Removal %)
Ion exchange method		74%	79%	66%
Softening method using	0.01 g/mL	23%	27%	16%
Leucobryum glaucum biosorbent	0.02 g/mL	59%	52%	71%

The methods that showed the greatest ability to remove the total hardness of the entire study are the ion exchange method (74% removal). Softening method using 0.02 g/mL moss showed also the ability to significantly remove the total hardness with 59% removal. The method of water softening using 0.01 moss showed the ability to soften water with a moderate reduction in total hardness where the hardness was reduced by 23%. The concentration of Ca^{2+}, as one of the most important parameters for the assessment of water hardness, showed the highest percentage of reduction after treatment by the method of ion exchange (79% removal). From the methods of water softening using moss, a significant percentage of Ca^{2+} removal had a setup using a mass concentration of 0.02 g/mL biosorbent in water with 25% removal. The method of water softening using 0.01 moss again showed the ability to soften water with moderate reduction (27% removal). Softening method using 0.02 g/mL moss proved to be particularly effective in removing Mg^{2+} from water, and more efficient than the ion exchange method with a percentage reduction in Mg^{2+} content of 71%. From the results, it can be concluded that, with this method, the content of moss in the water has a significant impact on the efficiency of water hardness removal. The ion exchange method showed a reduction in Mg^{2+} content of 66%. The method of water softening using 0.01 moss was performed with poor efficiency of reduction Mg^{2+} (16% removal). A significant decrease in pH value was observed in the ion exchange method where the pH was reduced to 2.68 value compared to raw water where the pH has 7.2 value, while neither of the moss softening method setups showed a significant effect on the pH value. Softening method using 0.02 g/mL moss showed a significant reduction in electrical conductivity with a reduction percentage of 43.1% while softening method using 0.01 g/mL moss and the ion exchange method showed an insignificant impact on the electrical conductivity parameter.

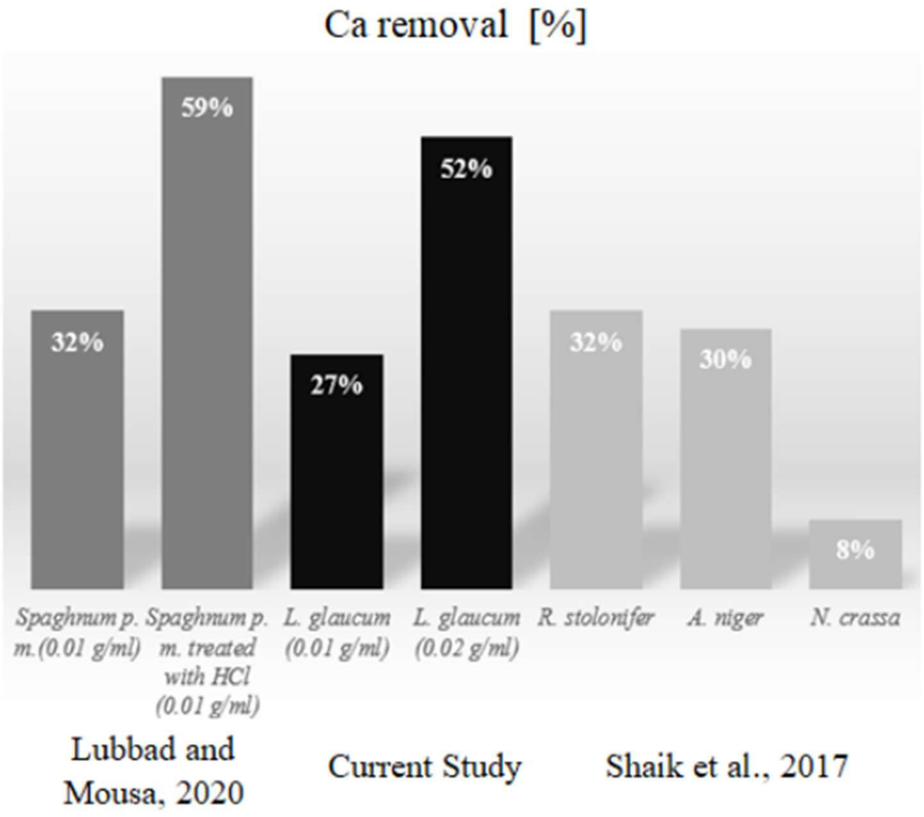


Figure 1. Percentage reduction Ca^{2+} biosorption method using *L. glaucum* compared to biosorbents used in previous studies [17,18]

Compared to the previous study [17], where Sphagnum peat moss was used, in which the percentage of Ca^{2+} 32% removal was achieved with the content of the mentioned biosorbent 0.01 g/mL and mixing time of 5 minutes, the moss softening method using *L. glaucum* showed a relatively small difference in terms of Ca^{2+} removal with the same moss content in water and mixing time compared to the mentioned study. The percentage of Ca^{2+} removal of pretreated Sphagnum is 59%, which is a significant increase. The study [18] also conducted research on

assessing the possibility of using microscopic fungal culture as a biosorbent with the species used: *Aspergillus niger* with 30% Ca^{2+} removal, *Neurospora crassa* with 8% and *Rhizopus stolonifera* with 32% (120 minutes sample preparation time). The results of Ca^{2+} removal using *L. glaucum* as a biosorbent in relation to other studies, in which other biosorbents were used in order to assess the efficiency of water softening, are shown in Figure 1.

4. CONCLUSIONS

During the laboratory tests, the ion exchange method, used as a reference method, showed the highest efficiency of hardness removal and Ca^{2+}, while the biosorption method where the moss content was 0.02 g/mL significantly removed the total hardness and Ca^{2+} as well. The method of water softening using 0.01 g/mL moss showed the ability to soften water with moderate to low reduction in total hardness, Ca^{2+}, and Mg^{2+}. Softening method using 0.02 g/mL moss proved to be particularly effective in removing Mg^{2+} from water, and more efficient than the ion exchange method.

The content of biosorbent (*L. glaucum*) in water in the biosorption method is a very important parameter and increasing the content of biosorbent significantly increases the efficiency of hardness removal.

Compared to the previous study [17] softening method using *L. Glaucum* with 0.02 g/mL content of biosorbent showed a relatively small difference in terms of Ca^{2+} removal.

Conflicts of Interest

The authors declare no conflict of interest.

References

[1] T. Kim, C. Park, E. Shin and S. Kim, Decolorization of disperse and reactive dyes by continuous electrocoagulation process, *Desalination*, 150 (2002), p. 165-175 https://doi.org/10.1016/S0011-164(02)00941-4

[2] A. Fathi, T. Mohamed, G. Claude, G. Maurin and B. A. Mohamed, Effect of a magnetic water treatment on homogeneous and heterogeneous precipitation of calcium carbonate, *Water Res*, 40 (2006), p. 1941–1950 https://doi.org/10.1016/j.watres.2006.03.013

[3] S. Seok-Jun, J. Hongrae, K.L. Jae, K. Gha-Young, P. Daewook, N. Hideo, L. Jaeyoung and M. Seung-Hyeon, Investigation on removal of hardness ions by capacitive deionization (CDI) for water softening applications, *Water Res*, 44 (2010), p. 2267–2275, https://doi.org/10.1016/j.watres.2009.10.020

[4] Y. Zeng, C. Yang, W. Pu and X. Zhang, Removal of silica from heavy oil wastewater to be reused in a boiler by combining magnesium and zinc compounds with coagulation, *Desalination*, 216 (2007), p. 147–159, https://doi.org/10.1016/j.desal.2007.01.005

[5] Y. Zarga, H. Ben Boubaker, N. Ghaffour and H. Elfil, Study of calcium carbonate and sulfate co-precipitation, Chem Eng Sci, 96 (2013), p. 33–41, https://doi.org/10.1016/j.ces.2013.03.028

[6] S. Lee and C. H. Lee, Effect of operating conditions on CaSO4 scale formation mechanism in nanofiltration for water softening, *Water Res*, 34 (2000), p. 3854–3866 https://doi.org/10.1016/S0043-354(00)00142-1

[7] M. K. Ahn and C. Haan, Technologies for the Removal of Water Hardness and Scaling Prevention, J. Energy Eng, 26 (2017), 23-29. https://doi.org/10.5855/ENERGY.2017.26.2.109

[8] T. W. Tee and A. R. M. Khan, Removal of Lead, Cadmium and Zins by Waste Tea Leaves, *Env. Tech. Letters.*, 9 (1988), p. 1223-1232, https://doi.org/10.1080/09593338809384685

[9] S. S. Nawar and H. S. Doma, Removal of Dyes from Effluents using low Costs Agricultural By-Products, Sci. of Tot. Enviro., 79 (1989), p. 271-279 https://doi.org/10.1016/0048-9697(89)90342-2

[10] D. C. Sharma and C. F. Forster, Removal of Hexavalent Chromium Using Sphagnum Peat Moss, *Water Res*, 27 (1993), p. 1201-1208 https://doi.org/10.1016/0043-1354(93)90012-7

[11] B. Sen Gupta, M. Curran, S. Hasan and T. K. Ghosh, Adsorption characteristics of Cu and

Ni on Irish peat moss, *J. Environ. Manage.*, 90 (2009), p. 954–960 https://doi.org/10.1016/j.jenvman.2008.02.012

[12] L. Ringqvist, A. Holmgren and I. Oborn, Poorly humified peat as an adsorbent for metals in wastewater, *Water. Res.*, 36 (2001), p. 2394–2404 https://doi.org/10.1080/00380768.2004.10408556

[13] Kłos, A. Gordzielik, A. M. Rajfur and Margorzata, Sorption of Cadmium and Zinc in Selected Species of Epigeic Mosses, *Bullet of Env. Contam. and Toxico*, 92 (2014), p. 323–328

[14] K. Orlanda Phytodegradation Effect of Leucobryum glaucum (Pincushion Moss) in a Source of Wastewater, *Ascend. Asia J. of Multidisci. Research*, 3 (2019) 2

[15] BAS EN ISO 10523:2008 Kvalitet vode – Određivanje pH vrijednosti, 1st Edition Institute for Standardization of Bosnia and Herzegovina, Sarajevo, Bosnia and Herzegovina

[16] AOAC, Official Methods of Analysis, 13th Edition, Association of Official Analytical Chemists, Washington DC, US.

[17] S. H. Lubbad and E. A. Mousa, Softening of tap water via calcium removal using sphagnum peat moss sorbent by batch and flowthrough approaches, *Internat. J. of Env. Stud.*, 77 (2020), p. 1-14 https://doi.org/10.1080/00207233.2020.1719805

[18] G. Shaik, L. Naveena and J. Latha, Converting of hard water to soft water using fungal bioremediation technology, *Depart. of Biotech.*, 3 (2017), p. 116-120 https://doi.org/10.12980/jclm.5.2017J6-192

JST&M 3(2022), 17 - 23
DOI: 10.57131/jstm.2022.3.3

Original scientific paper

INTENSIFICATION OF LOW-CARBON STEEL DESULPHURISATION IN THE INDUCTION FURNACE

Raza Sunulahpašić, Aida Imamović, Hasan Avdušinović

University of Zenica, Faculty of Metallurgy and Technology

ABSTRACT

Sulphur in steel is an undesirable element because it lowers all technological and uses values of steel products. During the steelmaking process, the desulphurization process depends on the thermodynamic conditions, the used desulphurizes, and the stability of the formed sulphides. The desulphurization technology in the production of low-carbon steel in a protective atmosphere, with the addition of synthetic slag and strong desulphurizing agents with additional argon blowing, is presented in this paper. The reduction of sulphur content achieved in the induction furnace is an important contribution to the technology of the production of low-carbon steels.

Keywords: desulphurization, induction furnace, synthetic slag, low-carbon steel

Corresponding Author:
Raza Sunulahpašić
Faculty of Metallurgy and Technology, University of Zenica
Travnička cesta br.1, Zenica 72000, B&H
Tel.: +387 32 401 831; fax: +387 32 406 903
E-mail address: raza.sunulahpasic@unze.ba

1. INTRODUCTION

Sulphur in steel occurs in all processes of production of liquid steel in lower or higher contents and is a harmful impurity because it reduces the mechanical properties, weldability, anticorrosive, electrical and other properties [1].

The harmful effect of sulphur is already expressed at the content of 0.005 – 0.010%, and in some cases at significantly lower values. Sulphur has unlimited solubility in liquid steel and very limited solubility in solid steel. Due to the reduction of solubility, during the solidification and cooling of steel, sulphur is excreted from the melt in the form of sulphide eutectic and collects at the grain boundaries. This eutectic has a very low melting point (988 °C) and is further reduced if oxygen is present in the eutectic, which leads to the appearance of eutectic type FeO-FeS (940 °C), which weakens the bond between grain and causes "red fracture".

To reduce the harmful effect of sulphur on steel properties, efforts are made to produce steel with the lowest possible sulphur content and with sulphide inclusions that have a predominantly globular shape and do not deform during hot plastic processing.

Sulphide and oxysulphide inclusions are deformed during hot processing and especially MnS inclusions spread in the longitudinal direction in the direction of rolling, which causes anisotropy of the steel properties.

The addition of calcium can affect the transformation of sulphide inclusions, with undesirable MnS inclusions being converted to CaS inclusions, while solid aluminates are transformed into liquid calcium aluminates. By injecting CaSi or Ca, modification and calcium sulphide are achieved. A minimum Ca/S ratio is required to achieve complete modification. In steels, these aluminates are covered with a thin layer of complex Mn and Ca sulphides, Figure 1.

With the increasing content of CaS in mixed crystals (Ca, Mn) S, there is an increase in sulphide hardness. In plastic processing, sulphides in which MnS predominates are deformed, while sulphides in which CaS predominates retain their original form, Figure 2. As the CaS content increases, toughness increases in all directions and increases the isotropic properties of steel.

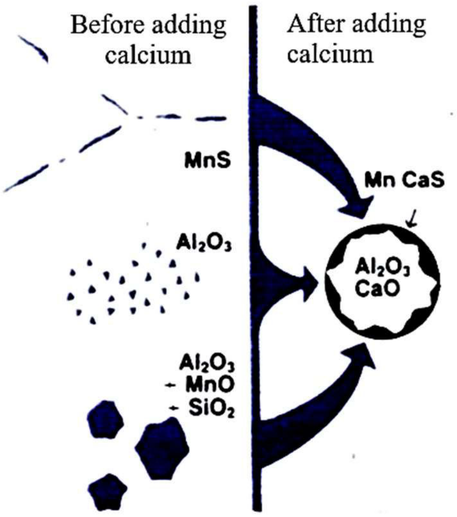


Figure 1. Schematic representation of the modification of the inclusions [1]

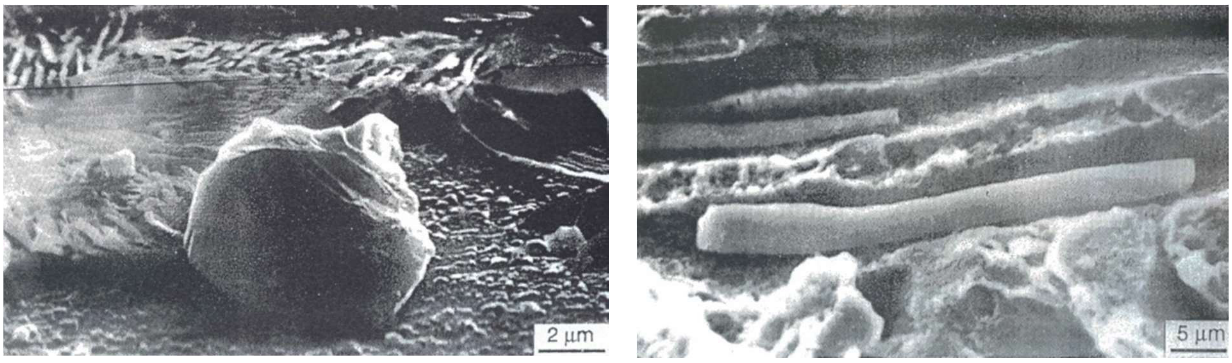


Figure 2. Morphology of sulphide inclusions in steel CaS (left) and MnS (right) [2]

In the integral production of clean steel, the control of sulphur content is of particular importance [3]. Desulphurization of steel implies optimization of the chemical composition of the slag using different agents, taking into account the increase in productivity and the reduction of production costs [4]. Most of the desulphurisation takes place through the reaction between magnesium and sulphur in the bath. The formed MgS ascends to the slag layer and reacts with lime to form CaS [5].

1.1 Technological procedures for sulphuring

The desulphurisation process depends on the thermodynamic conditions, the used desulphurizes and the stability of the formed sulphides. Achieving low sulphur contents in steel is not only a metallurgical but also an economic problem. Thermodynamic and kinetic conditions for good desulphurization are sometimes opposite to the realization of some other metallurgical processes, such as oxidation, phosphorus removal and others [6]. Conditions for good desulphurization are:

- high CaO activity;

- low oxygen activity;
- the ability of slag to dissolve CaS.

In addition to thermodynamic factors, kinetic factors are important for the desulphurization process, among which the most important are [7]:

- good slag fluidity;
- size of the contact surface between metal and slag;
- mixing intensity of metal and slag phase;
- influence of the gas phase.

2. EXPERIMENTAL PROCEDURE

The experimental part of this work was done at the Institute "Kemal Kapetanović" in Zenica, in the Department of Melting and Casting. The tests aimed to determine the effect of desulphurization agents as well as additional mixing of liquid melt with inert gas on the desulphurization efficiency [8].

The technology of making test melts in an induction furnace consisted of the following phases:

1. charge preparation;
2. charge melting;
3. sampling for chemical analysis of metals and slag, with temperature measurement;
4. removal of primary slag;
5. addition of synthetic slag;
6. blowing the melt with argon (5 min);
7. sampling for chemical analysis of metals and slag, with temperature measurement;
8. addition of strong deoxidants to the melt;
9. blowing the melt with argon (10 min);
10. sampling for chemical analysis of metals and slag, after 1 min of blowing, 5 minutes and 10 minutes;
11. monitoring the temperature during blowing and maintaining the temperature within the set limits;
12. pours melt into moulds.

An induction furnace with a capacity of 50 kg was used to prepare the starting material. The T-1 melt was made of low-carbon steel of the chemical composition given in Table 1.

Table 1. Chemical composition of starting material [8]

Melt	Chemical composition, %							
	C	Mn	Si	P	S	Cr	Ni	Mo
T-1	0.22	0.54	0.10	0.024	0.025	0.20	0.10	0.03

After cooling ingots (4.5 – 5 kg) were prepared from the starting melt for the re-melting in the vacuum induction furnace. The vacuum induction furnace with a capacity of 20 kg with a sintered magnesite refractory lining was used.

Argon purge was performed from above and desulphurization was achieved using synthetic slag and complex alloys of CaSiAl and CaSiMg.

Chemical composition (Table 2) is the most important characteristic of slag because it determines its basic physical and chemical properties. The composition of slag is determined based on the fact that the basic component is CaO as well as that the basicity of slag must be as high as possible, taking into account its viscosity at processing temperatures.

The best effect is in terms of reducing the sulphur content as well as oxygen observed in the treatment of steel with calcium [1]. Therefore, Ca-based desulphurizes (CaSiAl and CaSiMg) were selected, which were added in an amount of 1-3 kg / t. and their chemical composition is given in Table 3..

Table 2. Chemical composition of added synthetic waste [8]

Composition slag I			**Composition slag II**		
CaO	0.233 kg	64%	CaO	0.112 kg	32%
SiO_2	0.053 kg	14%	Al_2O_3	0.063 kg	18%
CaF_2	0.080 kg	22%	CaF_2	0.175 kg	50%
total	0.366 kg			0.350 kg	

Table 3. Chemical composition of desulphurizes

CaSiAl	60% Ca	30% Si	10% Al
CaSiMg	60% Ca	30% Si	5% Mg

Melting was performed under an argon atmosphere. Argon flow is turned on during the melting period to prevent oxidation of the steel melt.

After the raw materials for smelting are charged, melting is performed at maximum power. When all charges is melted, a sample was taken for chemical analysis. The formed amount of slag was removed, and after reaching the prescribed temperature, (1590 °C – 1610 °C), alloying was performed.

Melting and refining in the furnace were performed under the protection of argon. Argon was blown with 0.006 L/min through the asbestos-cement cover of the furnace. FeMn, FeSi and graphite were added through the same cover. The cover was removed when synthetic slag was added and when CaSiMg and CaSiAl were added using an immersion bell.

The chemical composition and temperatures of steel in an induction furnace and the final chemical composition of steel are shown in Table 4 as well as the chemical composition of slag in Table 5. The desulphurization process requires high basicity slag and reducing conditions.

Table 4. Chemical composition of steel and overview of measured temperatures [8]

MELT	Test	Temp. °C	Chemical composition of steel (%)					Synthetic slag
			C	**Mn**	**Si**	**S**	**P**	
V1	1	1610	0.20	0.91	0.30	0.037	0.017	SLAG I CaSiMg
	2	1615	0.19	0.91	0.14	0.019	0.017	
	3	1615	0.21	0.88	0.24	0.015	0.017	
	4	1610	0.22	0.85	0.21	0.014	0.017	
	5	1610	0.23	1.00	0.32	0.013	0.017	
V2	1	1600	0.18	0.65	0.21	0.027	0.019	SLAG I CaSiMg
	2	1600	0.27	0.69	0.20	0.027	0.019	
	3	1600	0.24	0.70	0.35	0.018	0.019	
	4	1600	0.27	0.70	0.33	0.014	0.019	
	5	1600	0.29	0.72	0.37	0.012	0.020	
V3	1	1600	0.25	0.55	0.15	0.038	0.020	SLAG I CaSiAl
	2	1560	0.24	0.52	0.08	0.036	0.023	
	3	1600	0.22	0.56	0.17	0.029	0.022	
	4	1615	0.22	0.61	0.14	0.016	0.024	
	5	1590	0.21	0.60	0.11	0.013	0.024	
V4	1	1600	0.25	0.72	0.18	0.032	0.022	SLAG I CaSiAl
	2	1590	0.23	0.69	0.20	0.020	0.024	
	3	1600	0.23	0.68	0.29	0.017	0.023	
	4	1600	0.23	0.69	0.29	0.015	0.024	
	5	1600	0.20	0.70	0.27	0.013	0.024	
V5	1	1580	0.28	0.68	0.30	0.033	0.018	SLAG II CaSiMg
	2	1600	0.24	0.66	0.12	0.020	0.018	
	3	1600	0.23	0.63	0.20	0.013	0.018	
	4	1600	0.22	0.62	0.21	0.012	0.019	
	5	1610	0.22	0.61	0.18	0.012	0.018	

Note: Test 1- after melting; test 2-slag and 5 min blowing; test 3- after adding desulphurizes and 1 min purging; test 4- after 5 min of purging; test 5- after 10 min of purging

Table 5. Chemical composition of slag

Melt	Chemical composition of slag (%)									Basicity
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	K_2O	Na_2O	B1
V1	14.80	2.49	7.32	0.13	6.16	9.60	59.30	0.02	0.09	0.65
V2	23.80	8.00	1.67	0.30	1.25	23.80	40.50	0.13	0.39	1.00
V3	22.30	8.70	1.03	0.32	1.22	24.00	41.80	0.10	0.39	1.08
V4	22.60	7.70	1.43	0.28	0.88	26.90	39.20	0.09	0.85	1.19
V5	13.10	27.40	2.86	0.11	1.73	14.20	40.50	0.02	0.09	1.08

According to Table 5, increased amounts of MgO are observed. MgO is regularly present in basic slag and mostly comes from the refractory lining. The content of total sulphur in slag by individual phases of the process is given in Table 6.

Table 6. Total sulphur content in slag

Sample	Total sulphur content in slag (%)					
	V1	V2	V3	V4	V5	V6
1	0.04	0.02	0.02	-	0.05	0.03
2	0.04	0.16	0.19	0.19	0.20	0.26
3	0.01	0.10	0.07	0.19	0.16	0.12
4	-	0.10	0.08	0.18	0.16	0.13
5	-	0.10	0.09	0.15	-	0.11

Data on the change of sulphur content by technological phases are shown in Figure 3. Figure 4 shows the initial and final sulphur content in low-carbon steel melts. The achieved desulphurization percentages of S are given in Figure 5, and the degree of desulphurization by individual technological phases is in Figure 6

Achieving a satisfactory degree of desulphurization has given input to the development of procedures for injecting powder reagents, usually based on compounds with Ca. By applying these procedures, the sulphur content can be reduced and deep desulphurization can be performed and the remaining sulphides and oxides are converted to a less harmful form.

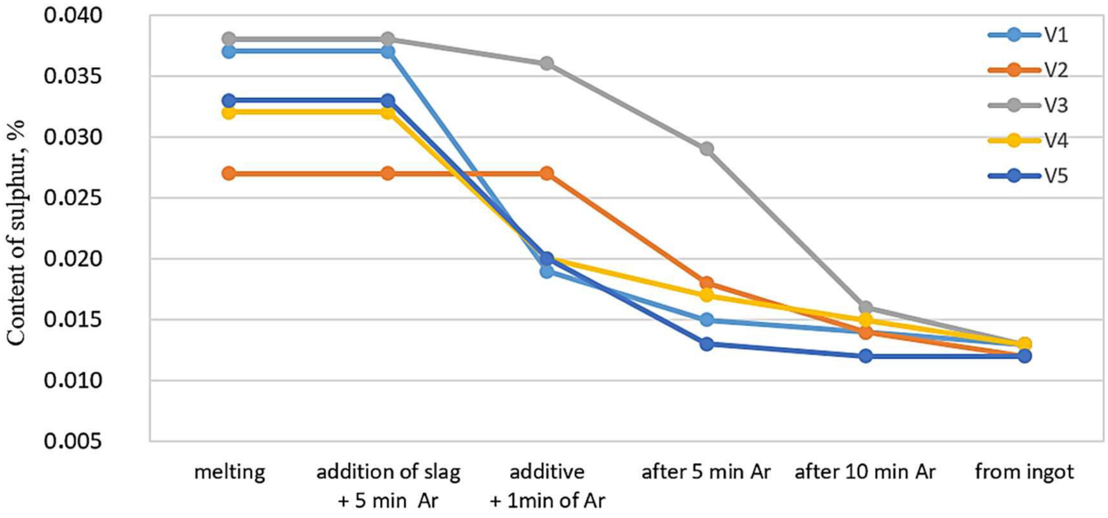


Figure 3. Change in sulphur content by individual melts of low-carbon steel quality

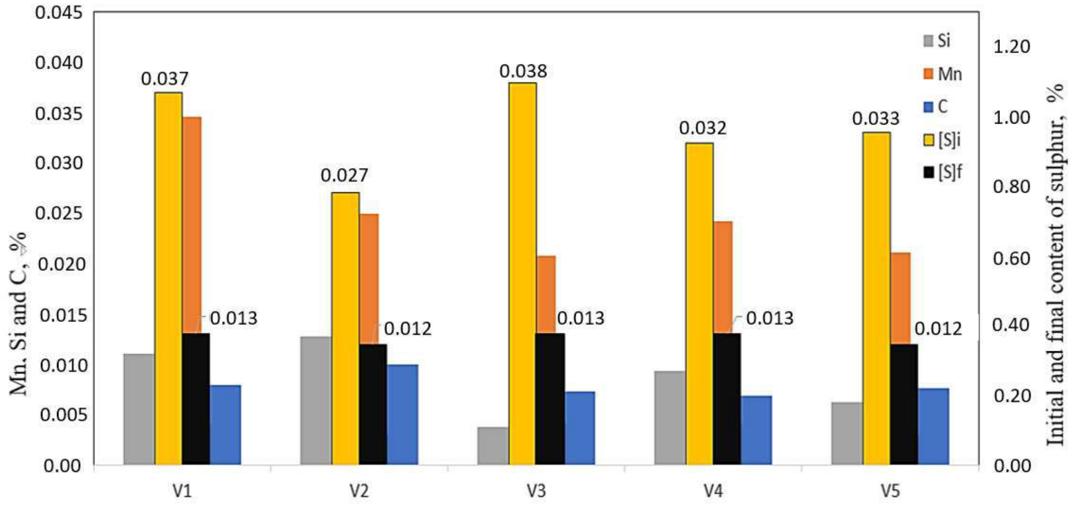


Figure 4. Initial and final sulphur content, C, Si and Mn content by melts

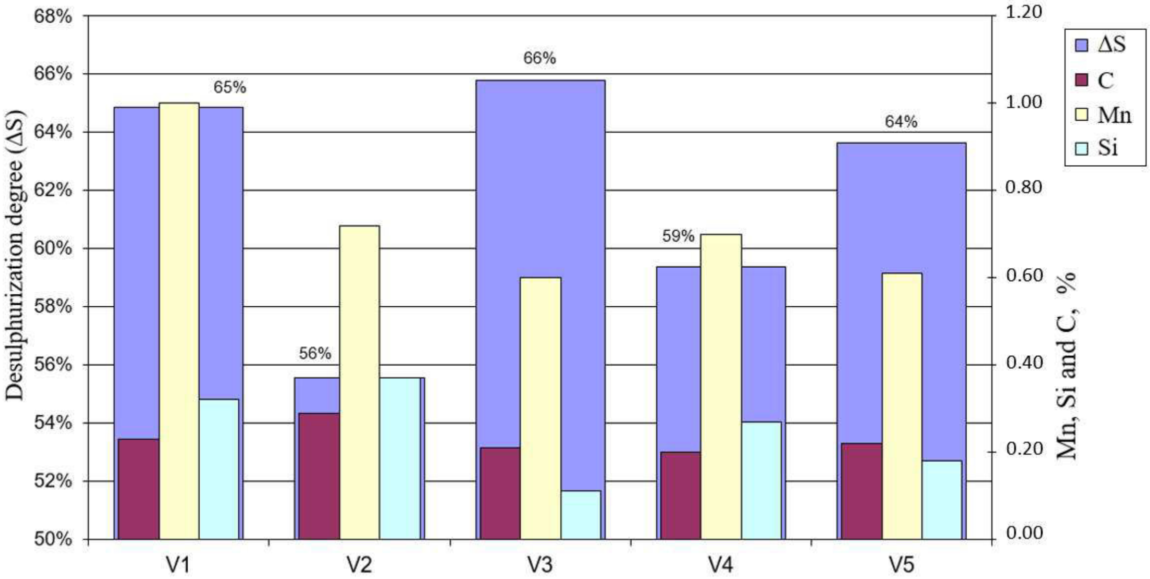


Figure 5. Realized percentages of S, Mn, Si and C in different low-carbon steel melts

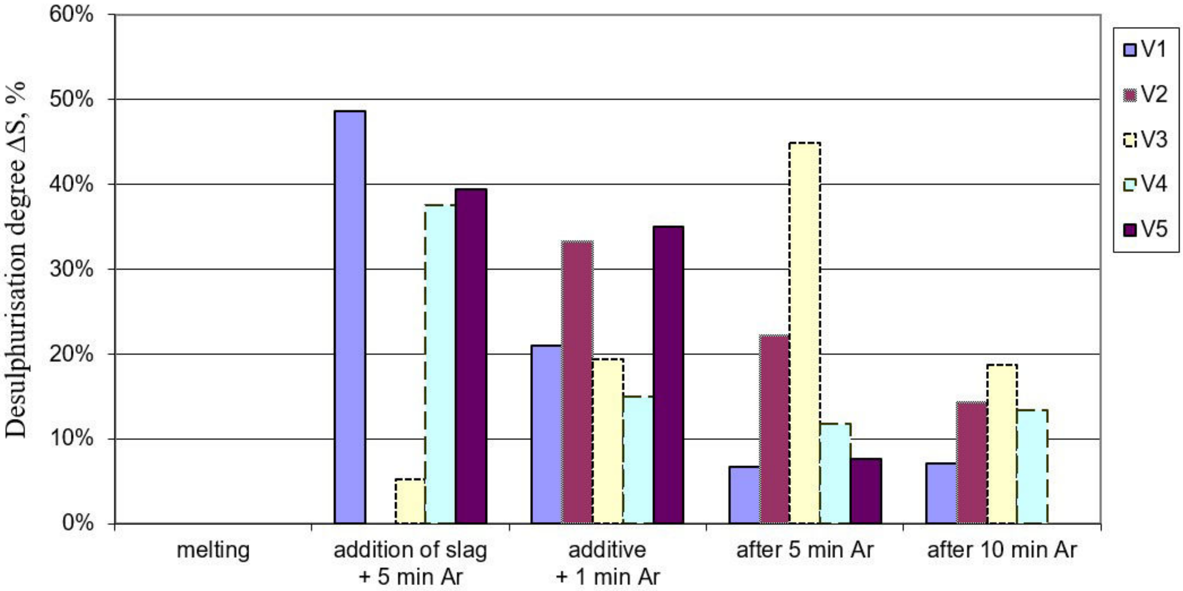


Figure 6. Desulphurization degree of individual technological phases

3. CONCLUSION

Practical research was realized in an induction furnace using basic refractory lining. The presented technology includes work in a protective argon atmosphere and the addition of strong desulphurizes (CaSiAl. CaSiMg).

The applied technology can effectively reduce sulphur in an induction furnace. The sulphur content in the metal, during the process, was reduced from 0.027-0.038% S to 0.012-0.013% S and the achieved average degree of desulphurization ranges from 56 to 66%.

The results of this research represent the contribution to the improvement of steel production technology from the aspect of desulphurization.

Conflicts of Interest

The authors declare no conflict of interest.

References

[1] Cored Wire: Available online: https://almatasia.com.my/casi-cored-wire/ (accessed on 04.04.2022.)

[2] A. Mahmutović, Š. Žuna, *Sekundarna metalurgija*, Fakultet za metalurgiju i materijale Univerziteta u Zenici, 2016.

[3] R. Hüsken, J. Cappel: Desulphurization strategies in oxygen steelmaking, *MPT Metallurgical Plant and Technology International*, 35 (2012) 5, p. 42-51

[4] D. Lindström, *A Study on Desulfurization of Hot Metal Using Different Agents*, [doctoral thesis], Department of Materials Science and Engineering, Royal Institute of Technology, SE-100 44 Stockholm Sweden, 2014

[5] F. N. H. Schrama, E. M. Beunder, S. K. Panda, H. J. Visser, E. Moosavi-Khoonsari, J. Sietsma, R. Boom, Y. Yang, Optimal hot metal desulphurisation slag considering iron loss and sulphur removal capacity part I: fundamentals, *Ironmaking & Steelmaking*, 48 (2021) 1, p. 1-13

[6] P. Pavlović, *Materijal čelik*, SKTH/Kemija u industriji, Zagreb, 1990.

[7] Z. Pašalić, *Metalurgija čelika*, Fakultet za metalurgiju i materijale, Zenica, 2002.

[8] R. Hadžalić, *Intenzifikacija odsumporavanja u indukcionoj peći uvođenjem nove tehnologije*, [magistarski rad], Univerzitet u Zenici, Fakultet za metalurgiju i materijale, Zenica, 2003.

JST&M 3(2022), 24 - 30
DOI: 10.57131/jstm.2022.3.4

Professional paper

INFLUENCE OF BORON, ZIRCONIUM, AND TELLURIUM ON THE IMPACT TOUGHNESS OF X8CrNiS18-9 STEEL

Derviš Mujagić[1], Aida Imamović[2] and Mustafa Hadžalić[1]

[1]University of Zenica, Institute "Kemal Kapetanović"
[2]University of Zenica, Faculty of Metallurgy and Technology

ABSTRACT

Steel X8CrNiS18-9 (standard EN 10088-3: 2005) is the most commonly used from the group of austenitic stainless steel in terms of machinability. The content of sulphur present in the steel from 0,15 to 0,35% has the exclusive task to improve the machinability. However, while sulphur improves machinability it simultaneously reduces the resistance of steel to corrosion but also affects the decrease in mechanical properties particularly steel toughness. Due to its harmful effect on the steel, as well as the fact that the non-metallic inclusions are insufficiently tested for this type of high-alloy steel the aim of this study is to determine the appropriate microalloying possibility to modify the non-metallic inclusions.

The aim of this work is that explore the influence of boron, zirconium, and tellurium on the impact toughness of the mentioned steel. Change of impact toughness, depending on the chemical composition of the steel is simulated with the Matlab program.

Keywords: impact toughness, boron, zirconium, tellurium, MATLAB

Corresponding Author:
Derviš Mujagić
University of Zenica, Institute "Kemal Kapetanović"
Travnička cesta 7, 72000 Zenica, B&H
Tel.: +387 61 588 883; fax: +387 32 247 980
E-mail address: dervis.mujagic@unze.ba; dervismujagic@yahoo.com

1. INTRODUCTION

Austenitic stainless steel X8CrNiS18-9 (EN 1.4305) also known as AISI 303 stainless steel has the best machinability of all steels of the same kind. The high content of sulphur or selenium in these steels improves their machinability. For this reason, they are produced only in the form of beams and rods and are used primarily in the mass production of screws. These types of steel are mainly used for less mechanically loaded parts because their toughness and dynamic durability are weaker than in other structural steels.

Of particular importance is to determine the behavior of nonmetallic inclusions in the process of manufacturing structural parts and in later exploitation. For this reason, it is planned to simulate the processing of austenitic stainless steel by plastic processing and by forging and rolling with two different degrees of processing. After that, the samples will be taken and laboratory testing of mechanical properties will be performed on them.

Research on the influence of microalloying elements boron, zirconium, and tellurium on the modification of non-metallic inclusions in austenitic stainless steel X8CrNiS18-9 with the aim of reducing their negative impact on the properties of this stainless steel, included research on a number of properties starting from machinability, corrosion resistance, microstructure, and mechanical properties.

In this paper, we will consider exclusively the influence of the above-mentioned elements on impact toughness [1-3].

2. EXPERIMENTAL PRODUCTION AND PROCESSING OF STEEL X8CrNiS18-9

2.1. Melting and casting

In accordance with the program of testing eight melts with various contents of boron, zirconium and tellurium were produced. Melting and casting of austenitic stainless steel X8CrNiS18-9 were carried out in a vacuum induction furnace with a capacity of 20 kg, maximum power of 40 kW.

The first melt was austenitic stainless steel X8CrNiS18-9 without any modifiers. After that, in the following seven melts, the composition was modified with the appropriate content of boron, zirconium, and tellurium, so that each of the mentioned elements was added independently, then in combinations with two, and finally with all three alloying elements.

Preliminary research determined the content of each individual microalloying element and they were added to each melt in the same amount as follows: FeB (0.002 kg), FeZr (0.020 kg), and MnTe (0.015 kg). The chemical analysis of all melt variants is given in Table 1.

Table 1. Chemical analysis of all melt variants [4]

Melt variants	Chemical composition (%)									
	C	Si	Mn	P	S	Cr	Ni	B	Zr	Te
Without alloying elements	0.03	0.42	0.61	0.021	0.18	18.3	9,4	–	–	–
Alloyed with B	0.05	0.47	0.66	0.021	0.19	18.5	9.5	0.004	–	–
Alloyed with Zr	0.04	0.35	0.75	0.021	0.17	18.8	9.4	–	0.016	–
Alloyed with Te	0.05	0.40	0.80	0.010	0.16	18.9	9.3	–	–	0.033
Alloyed with B and Zr	0.04	0.49	0.69	0.012	0.17	18.5	9.1	0.004	0.009	–
Alloyed with B and Te	0.04	0.35	0.78	0.011	0.18	18.8	9.3	0.004	–	0.039
Alloyed with Zr and Te	0.03	0.47	0.72	0.012	0.18	18.5	8.9	–	0.007	0.040
Alloyed with B, Zr and Te	0.04	0.44	0.78	0.012	0.19	17.1	9.3	0,006	0.012	0.042

2.2. Forging

After casting, all ingots are subjected to heat treatment: solution annealing – they are heated to a temperature of 1050 °C in a heating electric chamber furnace, and then quickly cooled in water.

After heat treatment, the samples were subjected to the forging on the press (Figure 1), and the final forging was done on an air hammer (Figure 2), approximately ∅ 50 mm. The set of samples after the forging process and the rough machining is shown in Figure 3.

2.3. Rolling

After forging and machining, the samples were subjected to a new degree of deformation by rolling. The first cross-section of the sample was reduced to □18 mm, and after the second passing through final sample dimensions were □14 x 50 mm. The rolling speed was 400 rpm. Figure 4 shows the all samples after the rolling process have been performed.

3. THE IMPACT TOUGHNESS

After completion of the forging and rolling process, the preparation for the impact toughness testing was started, and the geometry of the test sample is shown in Figure 5. The results of the test are given in Table 2.

Figure 1. Forging of ingots on a hydraulic press

Figure 2. Forging ingots on an air hammer

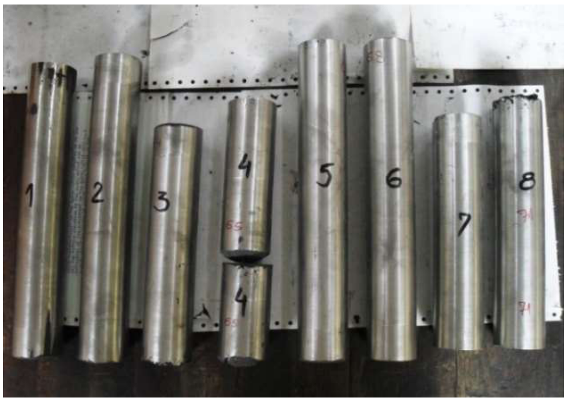


Figure 3. Samples after the forging process and rough machining

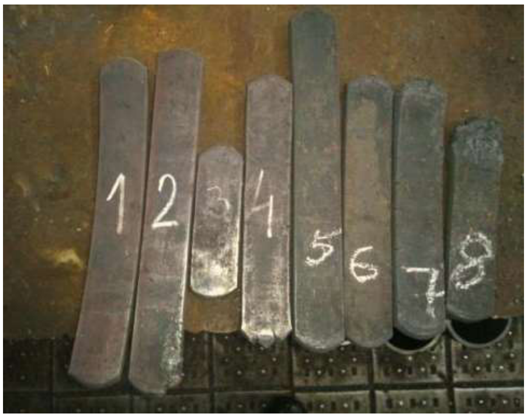


Figure 4. Samples after the rolling process

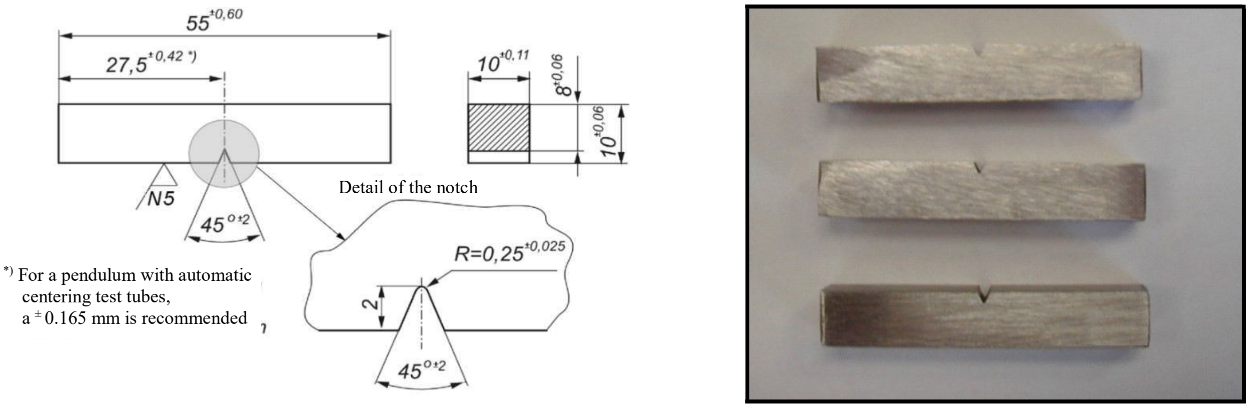


Figure 5. The shape and dimensions of the standard test samples for the impact toughness test

Table 2. Results of impact toughness test after the rolling process [4]

Melt variants	Impact toughness (J) KV 300 J	
	Individually (J)	Average (J)
Without alloying elements	60; 56; 56	57
Alloyed with B	48; 47; 59	51
Alloyed with Zr	55; 69; 55	60
Alloyed with Te	58; 69; 60	62
Alloyed with B and Zr	68; 69; 59	65
Alloyed with B and Te	75; 57; 71	68
Alloyed with Zr and Te	64; 69; 62	65
Alloyed with B, Zr and Te	57; 57; 63	59

4. STATISTICAL ANALYSIS OF EXPERIMENTAL RESULTS

In order to obtain a more complete insight into the existence of a connection between the obtained test results and the chemical composition, data processing for the obtained values of impact toughness was performed using MATLAB 7.0 [5] software package. The analysis was conducted in the way that functional dependency results of impact toughness with the basic parameters of boron, zirconium, and tellurium content were requested.

4.1. Determination of the regression curve for the impact toughness (KV)

The data for the observed indicators of the influence of the content of alloying elements of boron, zirconium, and tellurium on the experimentally determined values of the impact toughness is shown in Table 3.

Table 3. Impact toughness for different values of alloying elements [4]

Melt variants	B (%)	Zr (%)	Te (%)	KV_E (J)	KV_M (J)	Deviation (%)
Without alloying elements	0	0	0	57	54.651	-4.122
Alloyed with B	0.004	0	0	51	55.197	8.229
Alloyed with Zr	0	0.016	0	60	62.942	4.904
Alloyed with Te	0	0	0.033	62	64.549	4.110
Alloyed with B and Zr	0.004	0.009	0	65	59.861	-7.906
Alloyed with B and Te	0.004	0	0.039	68	66.894	-1.626
Alloyed with Zr and Te	0	0.007	0.04	65	62.542	-3.781
Alloyed with B, Zr, and Te	0.006	0.012	0.042	59	60.366	2.315

For the data from table 3, the regression coefficients, i.e. the regression equation (1), were calculated in the MATLAB software package:

$$KV_{M1} = 54{,}4716721 - 72{,}3501386 \cdot B + 454{,}8206726 \cdot Zr + 356{,}601515 \cdot Te + 103212{,}4804 \cdot B \cdot Zr - 16152{,}7494 \cdot B \cdot Te - 34383{,}21858 \cdot Zr \cdot Te \text{ ....(1)}$$

Adequacy of the model (1) was performed according to the Fisher criterion, where for the degrees of freedom $d_{freg} = 6$, $d_{frez.} = 1$ and the significance threshold $\alpha = 0.05$ tabular, or critical value $F_{(6,1,0.05)} = 233.97$ [6]. As the calculated value $F_{M1} = 0.378 < F_{Tab.} = 233.97$, the mathematical model for KV_{M1} is **not adequate**.

For the data in Table 3, in the MATLAB software package, the regression coefficients were calculated and a stepwise procedure was applied in order to determine the significance of the impact factors and their interactions. In this way, a mathematical model (2) was obtained. Table 4 gives the statistical characteristics of the given model (2).

$$KV_{M2} = 54.650654 + 136.564412 \cdot B + 518.223713 \cdot Zr + 299.934747 \cdot Te - 27619.486 \cdot Zr \cdot Te \quad (2)$$

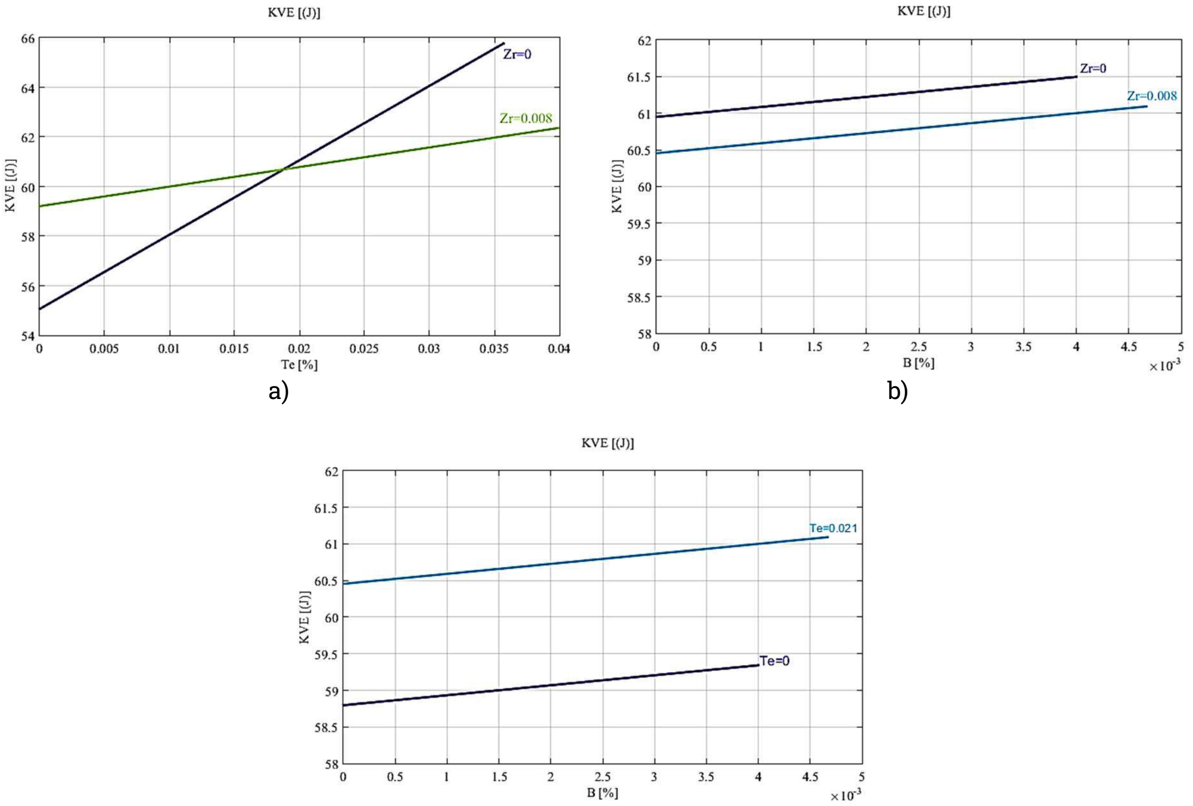
Table 4. Statistical characteristics of the impact toughness KVM [6]

KV_M	R^2	S_{ey}	$SS_{reg.}$	$SS_{rez.}$	F_{Mi}	F_{Tabi}	Significance
Condition after rolling	0.636	4.316	129.051	73.824	13.111	9.12	YES

The adequacy of the model (2) is checked by the Fisher criterion with degrees of freedom $df_{reg} = 4$, $df_{rez.} = 3$ and significance threshold $\alpha = 0.05$. Theoretically, the critical value from the corresponding Table is $F_{(4,3,0.05)} = 9.12$ [6]. Since the calculated value is $F_M = 13.111 > F_{Tab.} = 9.12$ the mathematical model for the impact toughness KV_{M2} is **adequate**.

Based on the obtained values of the correlation coefficients, conclusions were made about the nature and strength of the influence of individual independent variables, i.e. the most influential is the content of tellurium and zirconium, as well as the interaction of the influential factors of the first order zirconium-tellurium. Figure 6 shows a diagram illustrating the simultaneous influence of two factors on the objective function, for mathematical models of polynomial form (2).

From the position of the lines on the impact toughness diagrams, it can be concluded that the interaction between the influencing factors of zirconium and tellurium exists (Figure 6a), while such interaction between boron and zirconium and boron and tellurium, does not exist (Figures 6b and 6c).



a) b)

c)

Figure 6. Effects of interactions of combined factors on impact toughness [4]

The subsequent analysis required the functional dependence of the results of the impact toughness and the basic parameters of the content of boron, zirconium, and tellurium. Since the regression surfaces described in (2) can not be represented in a three-dimensional space, the regression variables are replaced by their average values. 3D models for different values of changing variables in the given interval are presented in Figure 7, for the mean values of the third component.

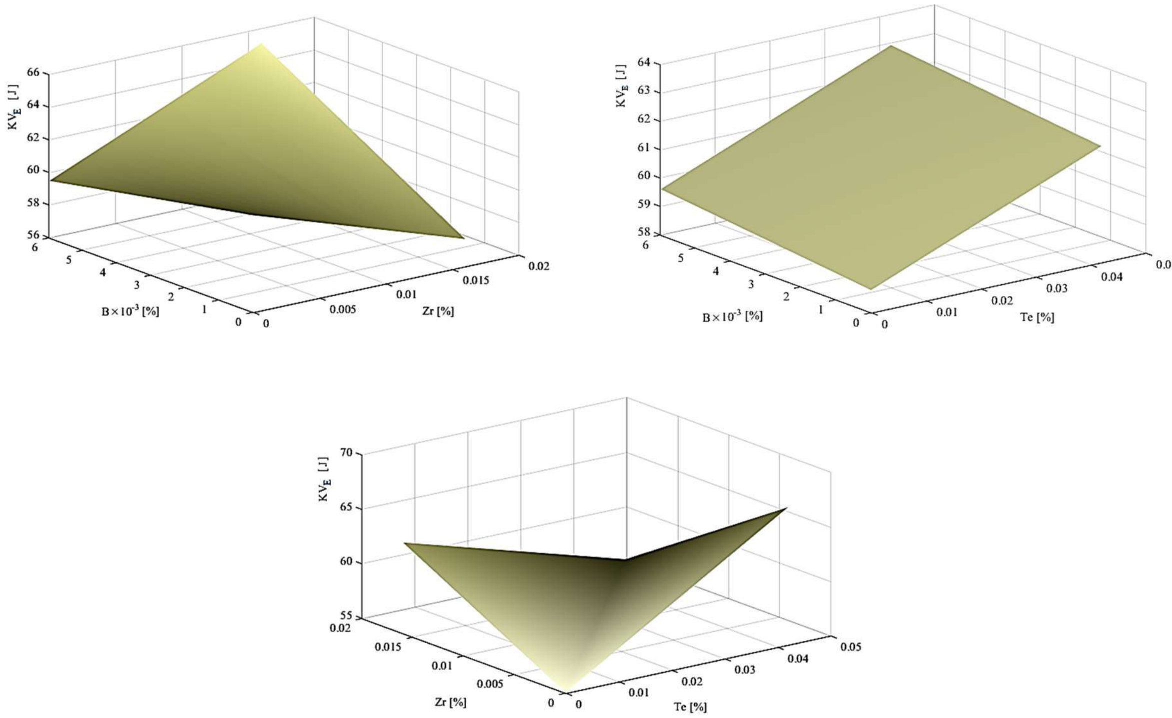


Figure 7. The functional dependence of the impact toughness on the content of B, Zr, and Te [4]

5. CONCLUSIONS

The objective was to determine the influence of boron, zirconium, and tellurium, on, the impact toughness of austenitic stainless steel X8CrNiS18-9 with the addition of sulphur.

Impact toughness tests were carried out in a rolled condition and the influence of chemical elements boron, zirconium, and tellurium on the impact toughness was monitored.

Based on conducted and experimental research, it is possible to make the following conclusions:

- An increase in the toughness value was observed in all variants of the melt, except for the melt alloyed only with boron, where a decrease in toughness was observed compared to the melt without alloying additions;
- The best combination of alloying elements in terms of increasing the toughness value is the combination of boron and tellurium.
- Based on the obtained results, it can be concluded that the addition of microalloying elements of boron (0.004 - 0.006%), zirconium (0.007 - 0.016%), and tellurium (0.033 – 0.042%) can improve the impact toughness of steel X8CrNiS18-9, especially in melt variants with combinations of the two said alloying elements.

Conflicts of Interest

The authors declare no conflict of interest.

References

[1] S. Kožuh, *Specijalni čelici* - skripta, Sveučilište u Zagrebu, Metalurški fakultet, Sisak, 2010.

[2] D. Mujagić, A. Mahmutović, M. Hadžalić, A. Karić, The influence of zirconium the machinability and impact energy of austenitic stainless steel, Proceedings of XIth Scientific/Research Symposium with International Participation "Metallic and nonmetallic materials: production-properties-application", Zenica, BiH, April 21st-and 22nd 2016

[3] D. Mujagić, M. Hadžalić, A. Imamović, M. Oruč, S. Muhamedagić, Influence of boron, zirconium, and tellurium on the mechanical properties of austenitic stainless steel, Proceedings of XIIth Scientific/Research Symposium with International Participation "Metallic and Nonmetallic Materials: production-properties-application", Vlašić, B&H, April 19th and 20th 2018, p. 43-48

[4] D. Mujagić*, Doprinos istraživanju uticaja mikrolegiranja sa borom, cirkonijem i*

telurom na osobine austeninog nehrđajućeg čelika sa dodatkom sumpora X8CrNiS18-9 [doktorska disertacija], Univerzitet u Zenici, Metalurško – tehnološki fakultet, Zenica, 2017.

[5] D. V. Lazić, M. R. Ristanović, *Uvod u Matlab*, Univerzitet u Beogradu, Mašinski fakultet, Beograd, 2005.

[6] S. Ekinović, *Metode statističke analize u Microsoft Excel-u*, Univerzitet u Zenici, Mašinski fakultet, Zenica, 2008.

JST&M 3(2022), 31 - 39
DOI: 10.57131/jstm.2022.3.5

Professional paper

THE INFLUENCE OF PROCESS PARAMETERS ON BROWN STOCK PULP WASHING AT NATRON-HAYAT MAGLAJ

Armina Čamić[1], Šefkija Botonjić[2]

[1]Natron-Hayat d.o.o. Maglaj.
[2]University of Zenica, Faculty of Metallurgy and Technology

ABSTRACT

Brown stock washing is one of the major unit operations within the pulp manufacturing business. Poor operating washers have the potential to significantly and negatively affect almost every other area of a pulp and paper mill, including the mill's environmental performance. The objective of the pulp washing is to remove the soluble impurities such as organic solids (lignin), fines, inorganic solids (Na, Mg, Ca, and K ions), and byproducts after each processing step. The present paper attempts to look at various parameters influencing pulp washing at Natron-Hayat Maglaj to ensure a complete understanding of the process. The results showed for this mixture of raw materials (15 % pine and 85 % fir) that the most influential parameters are Kappa number and dilution factor. Working with a high Kappa number above 50 requires additional equipment. Online control of the dilution factor would further improve the quality of the washing process and provide additional saving water and savings at the Evaporation plant. The First step for the future to improve the washing of unbleached kraft pulp is the optimization of the washing process through advanced control.

Keywords: pulp washing; wash loss; dilution factor, ,inlet and outlet consistency, pH, temperature

Corresponding Author:
Armina Čamić
Natron-Hayat d.o.o. Maglaj
Liješnica bb, Maglaj 74250, B&H
tel.: +387 62 857 664
E-mail address: armina.camic@natron-hayat.ba

1. INTRODUCTION

The objective of brown stock washing is to separate the product (cellulose fibers) from the process chemicals (black liquor), which mainly include alkali, sodium salts, lignin, and other chemically degraded wood components while using a minimal amount of wash water [1]. Reducing wash water results in higher black liquor solids, which in turn reduces steam demand in the evaporation process of the recovery cycle and increases energy recovery in the co-generation plant. In modern Kraft mills, usually, 96%-99% of the inorganic cooking chemicals are recovered back into the system. There are several variables affecting washing: dilution factor, inlet, and outlet consistency, pH, temperature, and entrained air. All these parameters relate to process conditions. Parameters such as mechanical pressure, fluid pressure (or vacuum), and particular traveling speed are considered equipment-specific parameters. Most of these parameters interact with each other and an improvement of one can differently affect the other [2].

The goal of the research is to identify important parameters visible on the Histograms, based on the results of the process management during three months of operation of the brown stock washing whose optimal management led to high-quality results in the washing line at Natron-Hayat.

1.1. Dilution factor

The dilution factors represent the net amount of water that is added to the washing system. The dilution factor is defined by considering the evaporation costs of black liquor, the manufacturing cost of fresh water, savings of condensates, losses of salt cake, losses of organic material, and treatment costs of the effluent treatment. Typically, the DF varies from 2-4.5 $m^3/_{\text{oven dry}}$ ton in the most relevant studies in this field [3].

1.2. Kappa number

The kappa number describes the amount of lignin remaining in the pulp after cooking – the higher the number, the higher the amount of residual lignin content. It should be noted that there is no general and unambiguous relationship between the Kappa number and the lignin content [4].

1.3. Inlet and outlet consistency of the pulp

Feed consistency plays an important role in the formation of the cake. If the consistency is too low, the pulp cake is too tightly packed, which deteriorates the washing liquid permeability. On the other hand, if the consistency is too high for the washer, the pulp cake might carry air thus declining the performance [5]. The Fiber consistency is found to decrease linearly with the cake thickness [4].

Design parameters for all washing equipment (inlet and outlet consistency) are given in Table 1.

1.4. pH value

In the weakly acidic region, reduced fiber swelling and improved dewatering can have a favorable effect on the washing process. Literature sources agree that maximum swelling of unbleached Kraft pulps is observed near the pH value of 9 [6].

Table 1. Design parameters for washing equipment [6]

Equipment for pulp washing	Inlet consistency (%)	Outlet consistency (%)
Continuous digester	10	10
Modified discontinuous digester	7-10	7-10
Diffuser	10	10
Wash Press	3-9	28-35
Pressure washer	3-4	12-14
Vacuum washer	1-2	12-14
DD washer	4-10	12-14

1.5. Entrained air

Prevention and elimination of entrained air are also important to maximize brown stock washing. Air trapped in the pulp also increases the drum speed by decreasing the stock drain ability and reducing the displacement ratio [7].

1.6. Wash liquor temperature

Liquor temperature plays an important part in influencing the viscosity of the washing liquor. For unbleached kraft pulp suspended in water between 20°C and 90°C, the rate of the leaching of lignin from the fiber wall increased with the temperature. From 20°C to 70°C, the change in the interfiber diffusion coefficient with temperature varied directly as expected for a diffusion process. Above 70°C, there was a much larger dependence of the diffusion coefficient on temperature than was observed at the lower temperature [8].

1.7. Specific parameters

Drum speed is another important variable when one is trying to achieve improved washing efficiency. Drum speed should vary as a function of vat level or sheet formation.

If the mat is too thick, it will carry over more of the dirty liquor because the shower water will not be able to fully displace the dirty liquid retained in the mat when it was formed on the drum. The thin mat will not provide good resistance to air penetration of the sheet into the liquor and the drum will tend to seal over, resulting in no drainage and no liquor displacement. The combination of drum speed and vat consistency should be the best available option when one is looking for a productivity increase [2]. Increased the rpm of the drum from 1 to 4 and found that the capacity of the drum increased by 2.5 times [4].

2. EXPERIMENTAL SECTION

The experimental work aims to monitor the influence of parameters on brown stock washing over a period of three months at Natron-Hayat. The experiments were carried out on a washing pulp line. The washing line consists of two stages of washing: washing pulp on a Rauma Repola drum washer (P = 38 m^2) that works under pressure and washing pulp on two vacuum drum washers ($P_1 = 35.3\ m^2$, $P_2 = 35.3\ m^2$). The experiments were carried out on softwood pulp samples containing 15% pine and 85% fir. The average Kappa number for all samples was 48. The cake was washed with hot water on the last drum washer. Flow, pressure, temperature, and level control are installed on the washing equipment. To obtain a realistic assessment of washing efficiency and alkali loss in the production of unbleached softwood pulp, the following research was conducted: sampling locations on the washing line were selected (at the output of the washers), measurements were made on laboratory devices and instruments in the Natron-Hayat laboratory according to ISO standards (the standard method of determining the Kappa number, consistency and wash alkali loss), research was carried out in industrially stable conditions of the brown stock washing at Natron-Hayat (optimal and stable production). Based on the obtained results it is important to see which parameters have the main effect on the Alkali loss, which is the main indicator of the quality of washing, and, based on that, propose measures to improve the pulp washing line.

3. RESULTS AND DISCUSSION

The effect of kappa number, dilution factor, wash water usage, temperature, number of rotations, outlet consistency, and alkali loss on the performance evaluation parameters is discussed. Histograms are added for better understanding and show, the underlying frequency distribution (shape) of a set of continuous data.

3.1. Kappa number

The Kappa number is one of the most important parameters measured in chemical pulping. The quality of pulp is also related to its Kappa number. The level of sobbed sodium varies with Kappa number and pH. Figure 1 shows the Kappa number from the digester. It indicates the pulp mill works with a higher unbleached Kappa number 47±3.

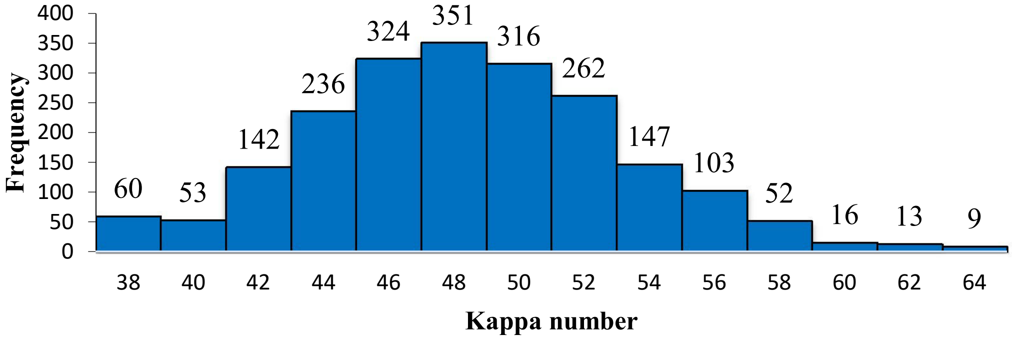


Figure 1. Kappa number of unbleached softwood pulp for the period of three months in 2022

Lower kappa-number pulping has two main limitations. The first is that pulping to lower kappa numbers can potentially damage pulp strength. The second is that, as delignification enters the residual pulping phase, the rate of carbohydrate dissolution becomes faster than the rate of delignification, resulting in a substantial loss in pulp yield. That is the main reason why the mill is working with a higher Kappa number but it also means that the mill needs better management of the washing process because Kappa number is a very significant factor in the washing process.

3.2. Wash water Usage

Figure 2 shows the Wash flow distribution in brown stock washing (m^3/t pulp). Wash water flow per ton of pulp varies over a wide range. Note that the specific wash flow generally drops as the production rate is increased.

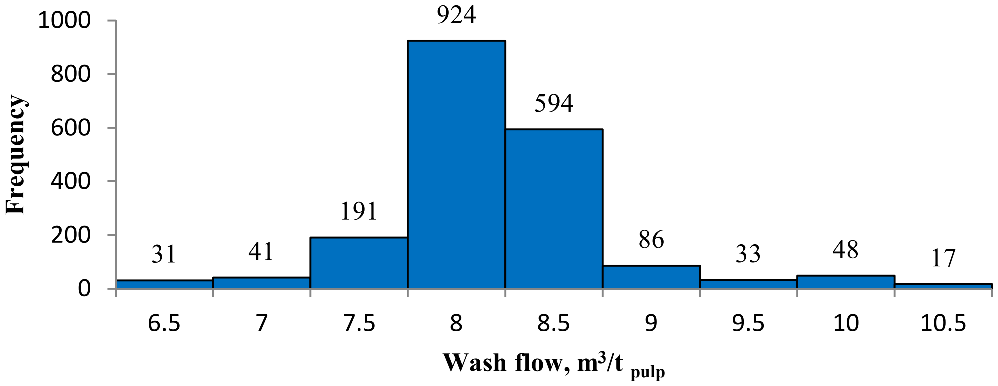


Figure 2. Wash flow distribution in brown stock washing for three months in 2022

3.3. Dilution Factor

Figures 3 and 4 show the dilution factor for the digester and the brown stock washing. Increasing the dilution factor improves washing results. On the other hand, when the dilution factor decreased below unity yielding a low washer performance. The dilution factor should therefore be above unity to guarantee unimpeded washer performance. However, the use of a dilution factor above two is not feasible, because the higher amount of wash water would increase the cost of black liquor evaporation.

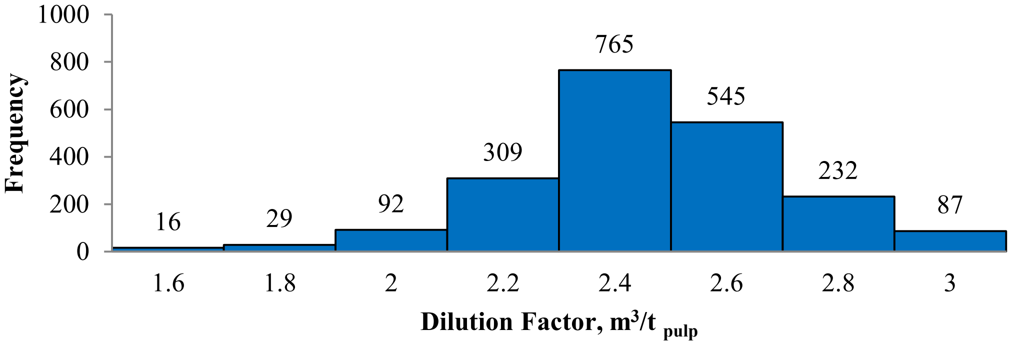


Figure 3. Dilution Factor in Kamyr digester for three months in 2022

Figure 3 shows a result of DF above 2 m^3/t pulp and it means good washing result in a first stage washing (Kamyr digester) and shows that the first step is well managed. Figure 4. Shows that result of DF at the last stage of washing is worse because the highest frequency of result is at 1.4 m^3/t pulp, which can affect the final washing result-the washing loss. Considering that the parameters are interrelated, this result may be the result of poor management of some of the parameters in the washing line (drum speed, level of production, liquid level).

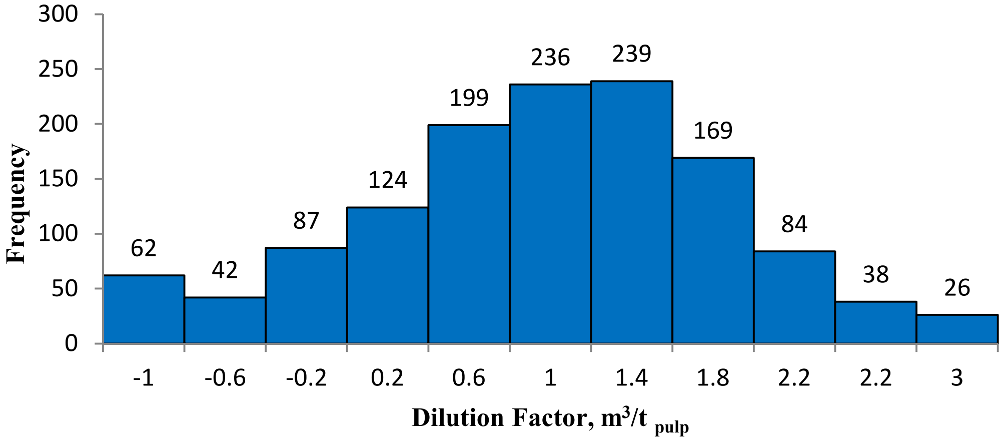


Figure 4. Dilution Factor in brown stock washing for three months in 2022

3.4. Temperature profile on brown stock washing

Figures 5-7 show the temperature profile on the washing line. At higher temperatures, viscosity is lower, less air remains in the pulp, the fiber pad is more porous, and foaming is less likely to occur. The effect of temperature on washing appears to be especially important in the pulping of pine and a little less so in spruce, presumably because of the larger size of the pits and larger relative pit area in pine parenchyma cells, which allow easier a toward diffusion of resin components.

Figure 5 shows the temperature of the filtrate used for washing in a pressure washer. This temperature is lower, which will affect the result of washing pulp from this washer, and if other parameters are not well managed, this impact on the result will be significant.

Figure 6 shows the temperature of filtrate used for washing on vacuum washer No. 2. This temperature must be high, near 70 °C. Because the washing result of this stage directly affects on total result.

Figure 7 shows the temperature of hot water used for washing pulp in the last stage of the washer. It is very important that the temperature of hot water be above 70 °C. On the Histogram, it is visible good distribution for temperatures.

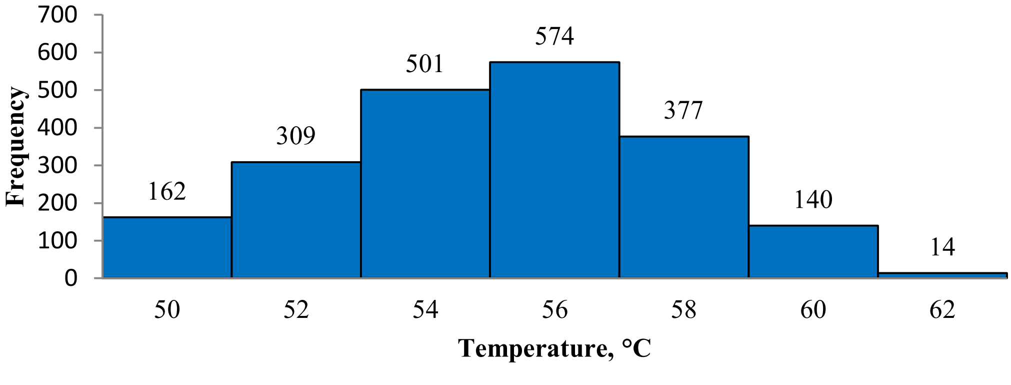


Figure 5. The temperature profile in the pressure washer for three months in 2022

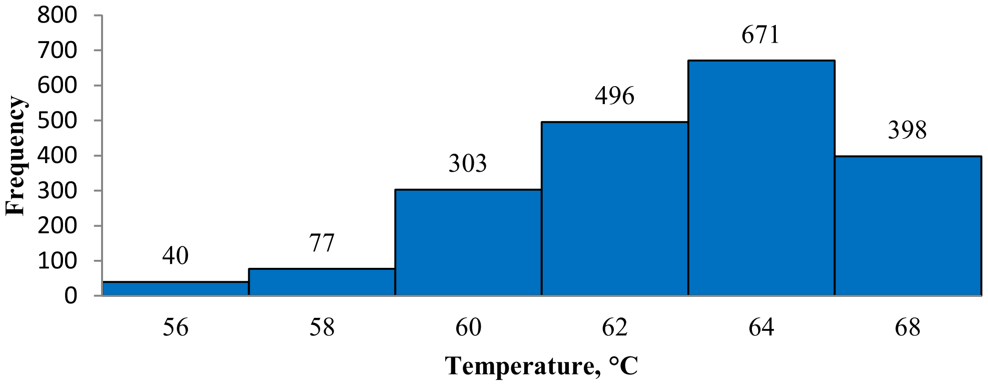


Figure 6. The temperature profile in vacuum washer No. 2 for three months in 2022

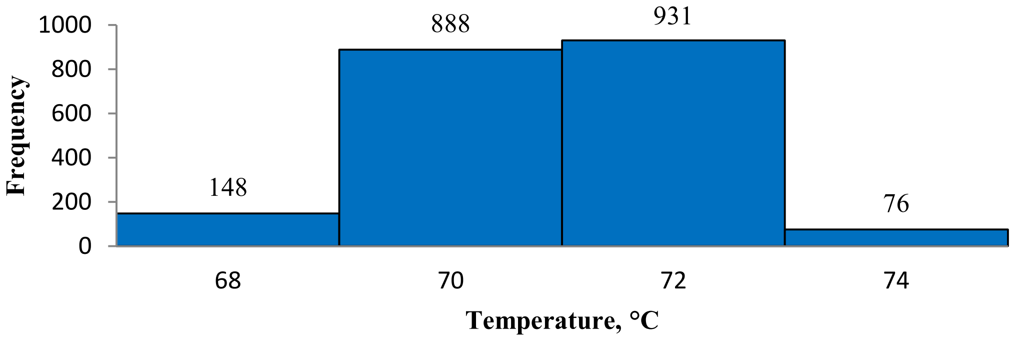


Figure 7. The temperature of water for washing on vacuum washer No. 3 for three months in 2022

3.5. Drum speed

Figures 8-10 show the number of rotation washers (Rauma Repola washer, vacuum washer No. 2, and No. 3). The pressure washer has a slower drum speed and it is normal for this equipment. It is expected that the same two vacuum washers have the same number of rotations but they do not, which will result in a different effect on washing loss. The optimal speed of the washer drum is very important for good washer results

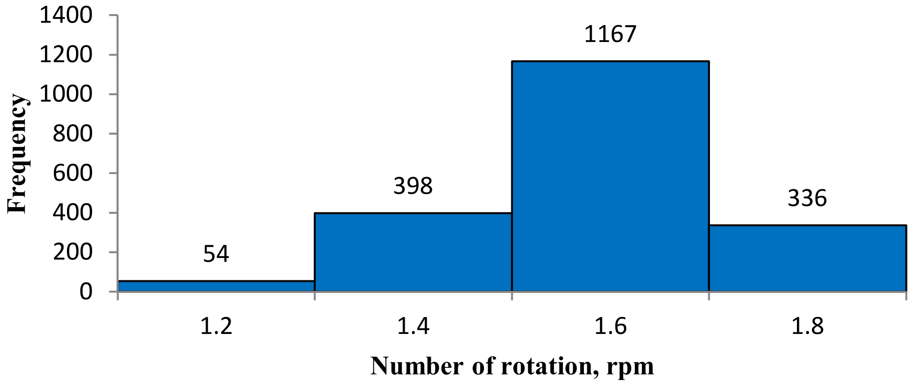


Figure 8. Number of rotation pressure washers for three months in 2022

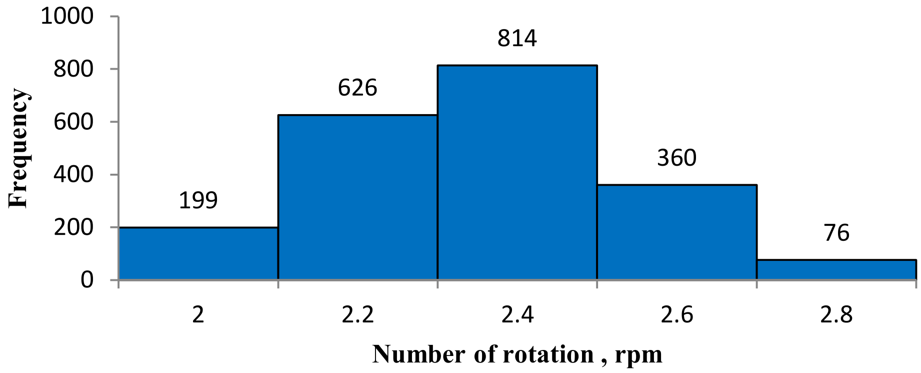


Figure 9. Number of rotation vacuum washers No. 2 for three months in 2022

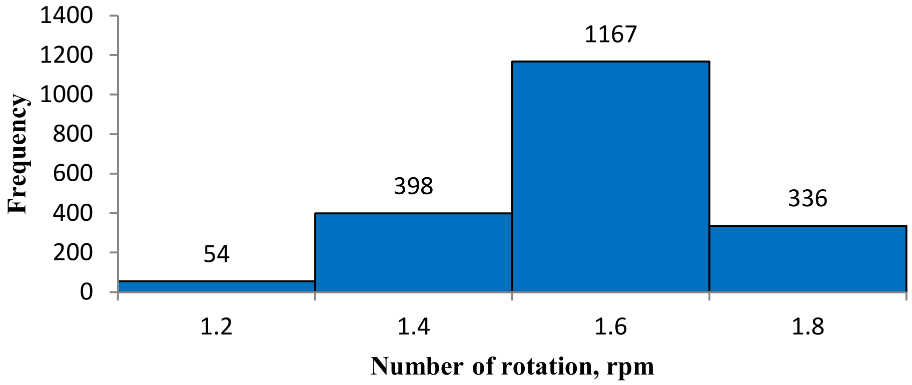


Figure 10. Number of rotation vacuum washers No. 3 for three months in 2022

3.6. Washer Outlet Consistency

Figures 11-13 show outlet consistency (pressure washer, vacuum washer No. 2, and No. 3). Washer performance is strongly dependent on the consistency achieved in the outlet pulp. Higher consistency means better drainage and lowers dissolved solids carryover.

Figure 11 shows the frequency of outlet consistency for the pressure washer and the result > 15% is a very good result for washing pulp on this type of equipment. Outlet consistency has the main effect on washing results and it depends on other parameters (DF, drum speed).

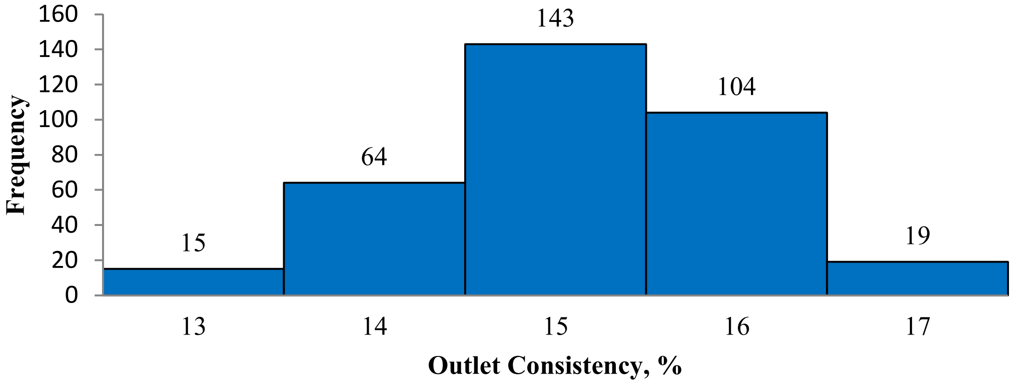


Figure 11. Outlet consistency (pressure washer) for three months in 2022

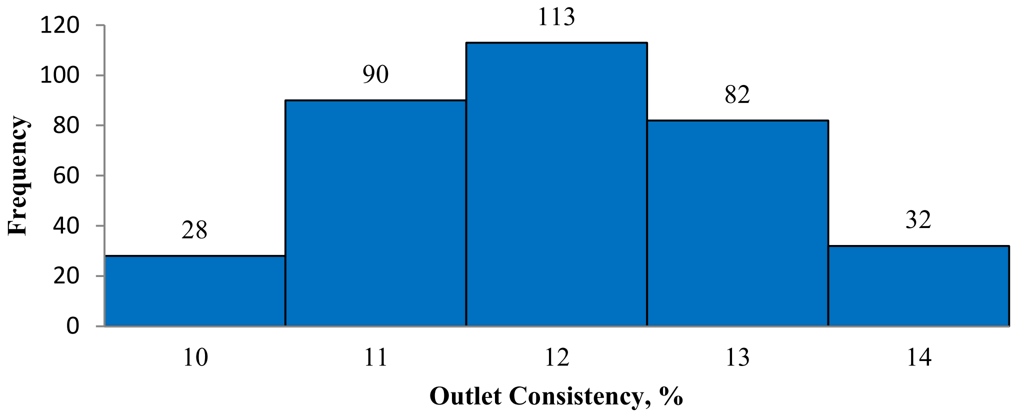


Figure 12. Outlet consistency (vacuum washer No. 2) for three months in 2022

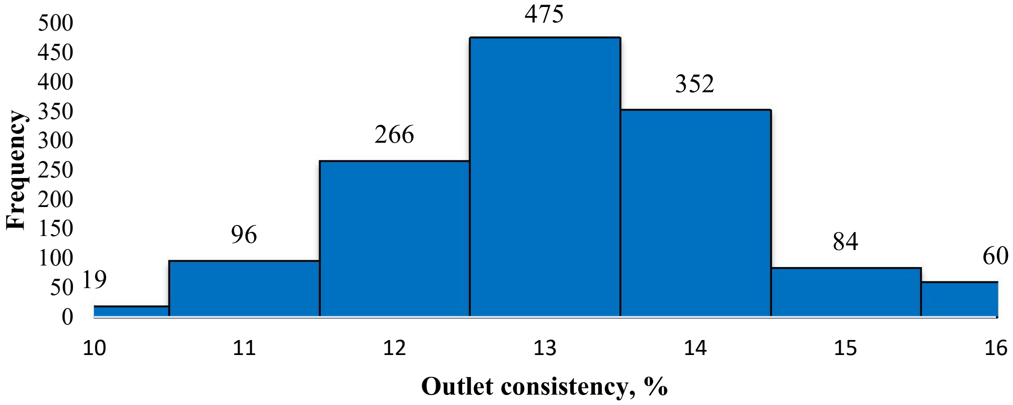


Figure 13. Outlet consistency (vacuum washer No. 3) for three months in 2022

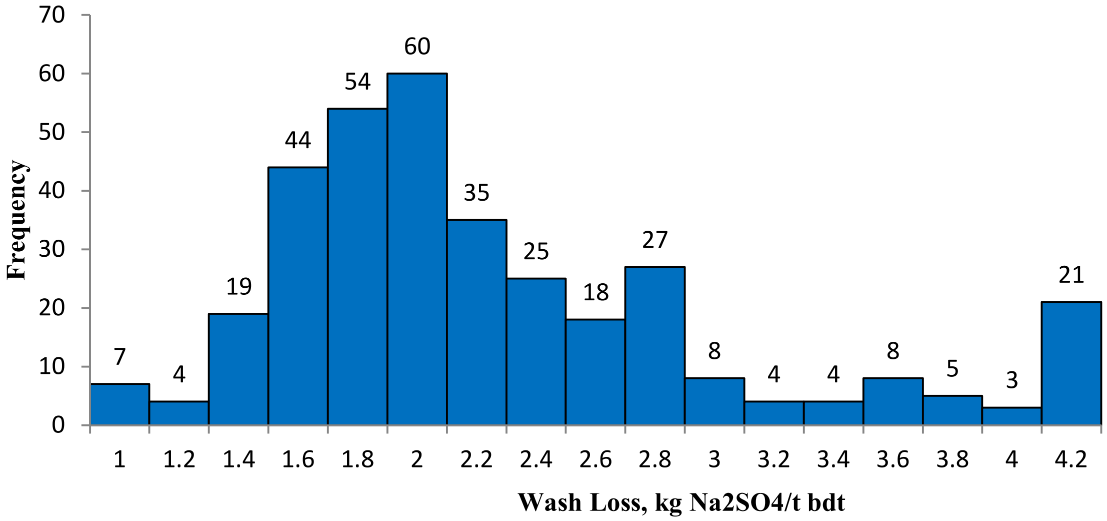


Figure 14. Wash loss (scan 37:98) for three months in 2022

Figure 12 shows the frequency of outlet consistency for vacuum washer No. 2 and consistency < 12% is not so good for this type of equipment. Figure 13 shows the frequency of outlet consistency for vacuum washer No. 3 and a consistency of 13% is a good and expected result for this type of equipment.

3.7. Wash loss

The Wash loss was measured every hour in the laboratory at Natron-Hayat. Wash loss is defined as the number of washable compounds in the pulp suspension which could have been removed in washing.

Figure 14 shows the amount of sodium in the pulp suspension after washing has typically been used as an indicator of wash loss, usually expressed as kg Na_2SO_4/oven-dry ton of washed pulp. From the Histogram, it is visible that 71% of very good pulp washing results but only 6% of results have a very significant negative impact on paper production. These results show good managed process brown stock washing with a high Kappa number.

4. CONCLUSION

The results obtained by experimental work showed that the process parameters did not affect or slightly affected the results of wash loss because they are guided and maintained by the technical standards of designed technological process equipment. It is completely satisfactory at all levels and complies with world standards for the given equipment. Because brown stock washing is one of the key aspects of a well-running integrated mill, reviewing and understanding brown stock washing fundamentals is important for all mill operations personnel. It is possible to affect and improve the carbon footprint of the product, partially the yield, chemical consumption (material efficiency), and water footprint (at least washing stages) by improving the washing efficiency.

Some optimum conditions for a rotary vacuum filter are:

- pH 9.5
- Temperature profile between 55-65 °C
- Rpm between 2.2-2.4
- Outlet consistency 13%
- The dilution factor is around 1.8

This results in low washing alkali loss between 1.8 and 2 kg $Na_2SO_4/t_{bdt.}$ This area is one of the key areas of improvement and investment thus ensuring technical efficiency of the overall pulp production process (washing efficiency, reduction of alkali loss, increase the quality pulp), improving environmental protection, improving the degree of regeneration chemicals, higher heat recovery, and ultimately affects the productivity, cost prices and profitability of the pulp mill. The results showed for this mixture of raw materials that the most influential parameters are Kappa number and dilution factor. Continuous working with a high Kappa number above 50 requires the addition of washing equipment. Online control of the dilution factor would further improve the quality of the washing process and provide additional saving water and savings at the Evaporation plant. The first step for the future to improve the washing of unbleached Kraft pulp is the optimization of the washing process through advanced control.

Conflicts of Interest

The authors declare no conflict of interest.

References

[1] R. Santos, and P. Hart, Brown Stock Washing –A Review of Literature, *Tappi Journal,* 13 (2014) 1, p. 9-19

[2] K. Gabov, *The effect of pulp washing on bleaching efficiency*, [Master´s thesis], Lappeenranta University Finland, Faculty of Technology, Lahti, 2009

[3] R. Kopra, E. Kari, M. Harinen, T. Tirri and D. Olli, Optimization of wash water usage in brown stock washing, *Tappi Journal,* (2011), p. 27-33

[4] V. K. Kukreja and J. Kumar, Rotary Brown Stock Pulp Washers through Mathematical Models -A Review, *Mathematical Theory and Modeling,* 2 (2012) 3, p. 43-51

[5] K. Koivula, *Improving the efficiency of brown stock washing line,* [Master´s thesis], Aalto University Finland, School of Chemical Technology, Espoo, 2014

[6] J. Kumar, V. K. Kukreja, Efficiency of Brown Stock Pulp washing in Liquid Properties. *International Journal of Engineering Science and Technology*, 3 (2011) 11, p. 8004 - 8011

[7] A. Mačković, *Uticaj procesnih parametara na gubitak alkalija u proizvodnji nebijeljene četinarske celuloze*, [magistarski rad], Tuzla, Tehnološki fakultet u Tuzli, 2016.

[8] B. D. Favis, J. M. Willis, D. A. I. Goring, High Temperature Leaching of Lignin From Unbleached Kraft Pulp Fibers, *Journal Wood Chemical Technology*, 3 (1983), p. 1–**7**